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The Deposition and Fate of Trace Metals in Our Environment

Symposium Proceedings

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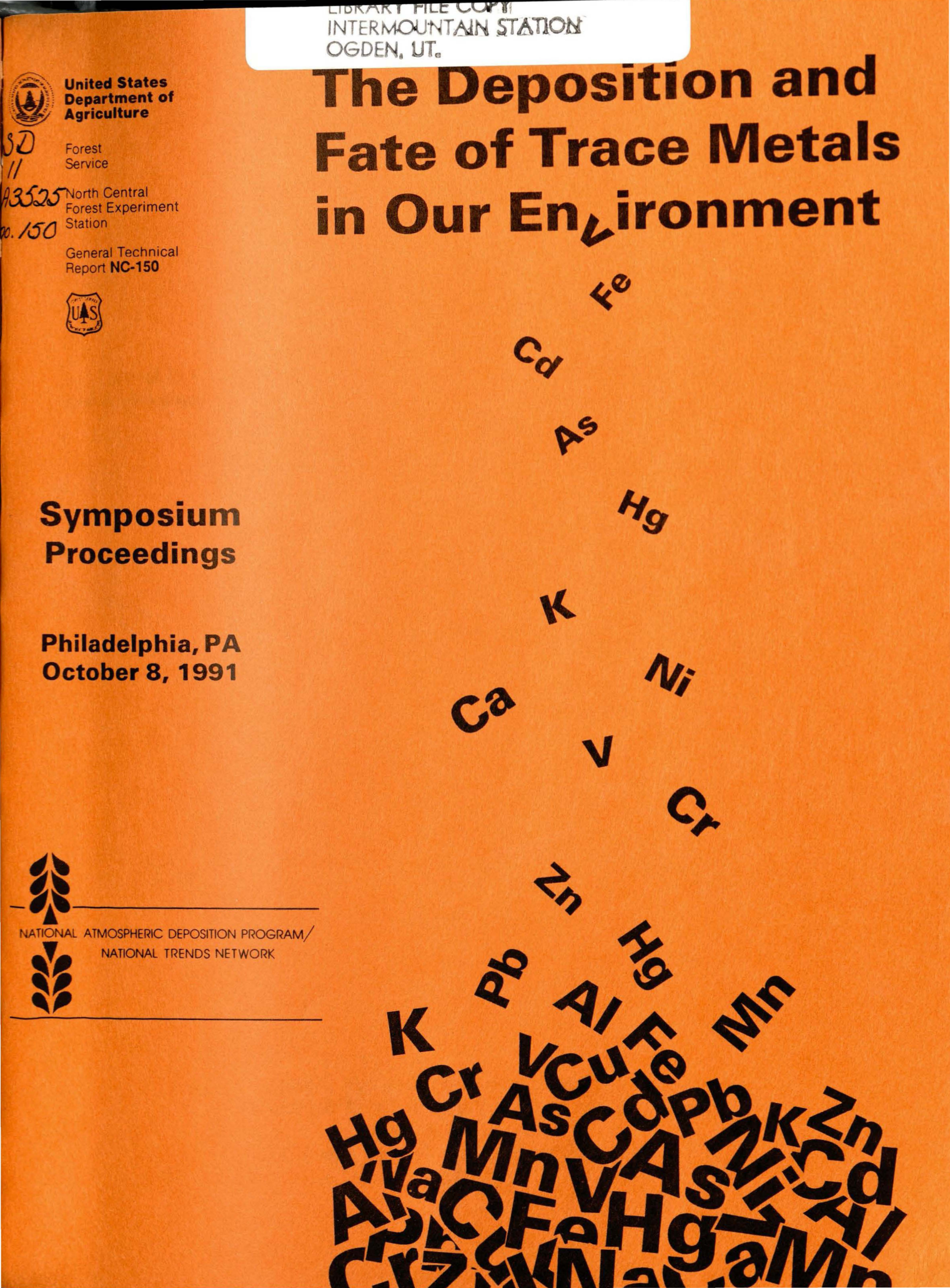
October 8, 1991



NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/
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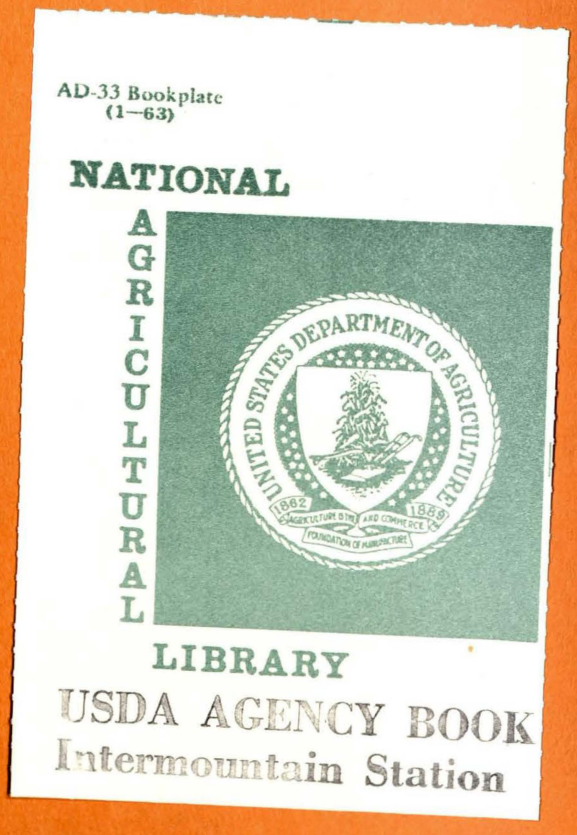

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The Deposition and Fate of Trace Metals in our Envrionment

Philadephia, Pennsylvania
October 8, 1991

Elon S. Verry
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Editors

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FORWARD

It is the business of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) to define the chemical climate of America. Since 1978, we have built a consistent, high quality record of the major anions and cations in precipitation nation-wide. A record used by scientists to better understand acid rain processes and impacts and used by legislators to define our national policy. Our chemical and data analysis is streamlined to deliver information in a timely and quality-controlled manner. The network has matured in area coverage and data management. We now seek to explore the addition of other critical environmental measurements. Among which are ultraviolet beta light, herbicides, and trace metals.

On October 8, 1991, in Philadelphia, the NADP/NTN Technical Committee hosted a symposium on the deposition and fate of trace metals in our environment. Fourteen papers were prepared by 37 authors with a breadth of experience in trace metal ecology over the last decade. These proceedings are meant to inform our members of the analytic and collection methods for trace metals in precipitation, and the processing of trace metals in the landscape and its biota. It is a solid review of trace metals designed to facilitate an informed discussion about the addition of trace metals to the NADP/NTN network.

We realize that rapid change in our world society and change in our environment is, in fact, the order of our world. However, this symposium helps us to see that change does not separate us from our past. Indeed, we have the opportunity to mold the future if we can interpret our historical legacy and monitor our present. The cycling of trace metals is part and parcel of our society and our environment. A recent vision of ecology in the 21st century[1] captures the need to understand the ecology of trace metals in our environment too.

> **"To treat Nature as a partner, people must learn, and learn well, the principles of ecology..., and see [the] implications not only for natural ecosystems but also for our own artificial and intensely human societies."**

NADP/NTN is well prepared to provide new services in a changing world. John Masefield in his poem "The Ending" from *The Wanderer* looks well beyond the end of the traveled road.

> **"Adventure on, for from the littlest clue**
> **Has come whatever worth man ever knew;**
> **The next to lighten all men may be you."**

Elon S. Verry

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[1]Eville Gorham, 1990. An ecologist's guide to the problems of the 21st century. The American Biology Teacher. 52(8):480-483.

THE DEPOSITION AND FATE OF TRACE METALS IN OUR ENVIRONMENT: A SUMMARY[1]

Elon S. Verry and Stephen J. Vermette[2]

A GLOBAL PERSPECTIVE

The actions of our global society now dominate the natural biogeochemical cycle of some trace metals in the atmosphere and many receiving ecosystems. The ratios of anthropogenic to natural fluxes of trace metals to the atmosphere are currently estimated at 28 for lead (Pb), 5 for cadmium (Cd), 3 for zinc (Zn) and vanadium (V), 2 for nickle (Ni) and arsenic (As), and about 1 for mercury (Hg), and copper (Cu). Energy production, and mining (including smelting and refining) are significant sources for all trace metals. Waste incineration also accounts for about half the amount of Hg emitted. Lead emissions are dominated by volatile losses from gasoline, but even without leaded gasoline, the ratio for Pb is 7. The magnitude of emissions and deposition rates are closely related, creating profound regional differences across the globe. The greatest perturbation of the natural trace metal cycle is in the northern hemisphere where most industries are located. The maximum difference in deposition is between the North Atlantic and South Pacific oceans. The most striking trend is a sharp rise in emissions and ambient environmental concentrations in developing countries, as opposed to declines in developed counties (See Nriagu).

THE LEGISLATIVE PERSPECTIVE

The 1970 Clean Air Act dealt primarily with national ambient air quality standards (NAAQS) for particulate matter, lead, sulfur dioxide, nitrogen oxides, ozone, and carbon monoxide. These standards are directed at threshold levels below which there are no adverse human health effects in populated urban areas. The 1990 Clean Air Act continues to focus on urban areas, but expands the need for ambient air quality measurements by mandating research in rural areas, and by extending the initial focus on human health to include effects on water, soils, forests and crops. Characterization of the spatial and temporal impacts of trace metal and toxic compounds on rural ecosystems is a significant part of the 1990 Clean Air Act Amendments. Title III,

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[1]Many of the words in this summary are paraphrased from the authors' manuscripts published in this proceedings. In this summary they are recognized for all or part of each paragraph.

[2]USDA-Forest Service, 1831 Highway 169 East, Grand Rapids, MN 55744; and Illinois State Water Survey, 2204 Griffith Dr. Champaign, IL 61820.

Section 112 (k)(2) calls for research to monitor metals, pesticides and many other hazardous air pollutants, and to characterize their sources and risks to public health in urban areas. Section 112 (m) requires EPA and NOAA to extend research and monitoring programs to the rural watersheds of the "Great Waters" including the Chesapeake Bay and coastal waters, and Lake Champlain, as well as the Great Lakes. Title IX, Section 901 of the 1990 Clean Air Act Amendments identifies new environmental and ecosystem measurement and monitoring research objectives on a national network basis. These objectives include evaluating the effects of air pollution on water quality, forests, materials, biological diversity, soils and crops. (See Pahl, et al.).

AN HISTORICAL PERSPECTIVE

PRIOR TO THE TWENTIETH CENTURY

The extraction and dating of lake sediment and peat cores suggests that rates of Pb deposition in the United States accelerated in the mid 1800's (See Norton and Kahl); however, ice cores from Greenland are longer and extend further back in time. They suggest that low rates of anthropogenic lead deposition in North America began in the mid 1700's. Lake and peat core analyses from Scotland, Norway, Finland, and Denmark suggest that trace metals released from industries in Britain and central Europe were reaching remote areas of Scandinavia by the mid 1600's . While local metal contamination of the environment existed near the silver mines of ancient Greece, long range transport of trace metals in the atmosphere probably began in the mid 1500's with the development of large smelting furnaces and tall stacks (see Nriagu).

THE TWENTIETH CENTURY

The highest rates of Pb accumulation in sediments began about 1960 in the United States. Norton and Kahl's analyses point out many of the problems associated with the interpretation of Pb chemistry in dated lake and peat cores. These include: uncertainties in sediment dating, coring difficulties, bulk or extractable methods of preparing sediments for chemical analysis, area-variable sedimentation processes, and sediment mixing by worms. Other problems include relocation of trace elements within the sediment, deposition of metals in sediment not of the same age, loss of trace metals from sediments caused by changes in oxidation state etc., and retention of metals within the catchment. For these reasons, the correspondence between measured air quality, atmospheric deposition, and sediment accumulation is useful for identifying historic changes and trends in only the broadest way (See Norton and Kahl).

Lead in the forest floor (organic material lying over the mineral soil) has been used to estimate Pb deposition directly. This method assumes that, once deposited, Pb is retained in the forest floor, and that there is no uptake or cycling of the Pb by vegetation. During the period of the mid 1960's to the mid 1980's, Pb deposition in the northeastern U.S. was estimated at 175 to 600 $g\ m^{-2}\ yr^{-1}$ increasing as elevation increased from about 500 m to 1000 m. However, repeated

measures of Pb in the forest floor, over the same period and in the same locations, show lower amounts of Pb at the end of the period. The amounts are even lower than that expected from reduced Pb deposition rates as unleaded gasoline replaces leaded gasoline. This leads to speculation that Pb is lost from the forest floor. The mechanism of loss is not confirmed, but may relate to the export of Pb bound with organic carbon in tea-stained leachate waters. Nonetheless, forest floor estimates of Pb deposition are similar to total (wet plus dry) Pb deposition measured at the mid-Atlantic coast in the early 1980's (400 g m^{-2} yr^{-1}) (See both Friedland, and Church, et al.).

Trace metals in the atmosphere are delivered to and are partially retained in receiving ecosystems. The work by Nater, et al. clearly shows a significant correlation between the deposition of S, and its concentration in various components of forest ecosystems from northwestern Minnesota to Michigan's Lower Peninsula . Sulfur in the forest floor, surface mineral soil, and in tree wood follows the increasing deposition of sulfur from west to east. The concentrations of Pb, Cd, and Hg in the soil components follow a similar gradient trend as S in those components. Trace metals and sulfur are often derived from the same industrial sources, and rural as well as urban ecosystems must process these elements along with sulfur. In present-day ecosystems trace metals are not merely sequestered in depositional sediments, but occur in the major ecosystem components in a dynamic fashion that corresponds with site specific atmospheric deposition from long range transport. (See Nater, et al., and Nriagu).

MEASURING REGIONAL TRACE METAL DEPOSITION

The Ontario Ministry of the Environment has measured Cu, Ni, Pb, Mn, Zn, Cd, Fe, Al, V, and As in wet-only deposition since 1981. High concentrations are located around and south of the lower Great Lakes. Annual loadings of Pb, Mn, Zn, and Cd to Lakes Ontario, Erie, and Huron show an annual rate of decrease from 1981 to 1988, averaging about 6%. This is true for Zn and Cd over Lake Superior as well, but annual Pb and Mn loading to Lake Superior has increased by 2%and 6% respectively (See Orr, et al.). With the exception of Ca and Na, similar trends are shown for the Great Lakes in the EPA GLAD network for the period 1982-1989. The most dramatic decrease in Pb deposition occurs near urban sites (See Klappenbach).

Trace elements have been measured in precipitation and aerosols at several mid-Atlantic coastal sites since 1982 by the University of Delaware as part of the NOAA-WATOX program. These data for 13 trace metals suggest common emission sources from the midwest and southeast U.S. with efficient precipitation scavaging after long-range transport. The atmospheric flux of most trace metals dominate the input of metals to coastal watersheds, and the export of metals from estuaries to coastal waters. Wet-only deposition accounts for 85% to 98% of the total atmospheric deposition of Cu, Zn, Ni, and Cd, and 47% to 55% of the total atmospheric deposition of Cr, Pb, and Fe. (See Church, et al.).

ACCURACY OF TRACE METAL MEASUREMENTS

Most of the trace metal concentrations reported for precipitation prior to 1980 are compromised by gross contamination, or conversely, by irreversible losses of certain metals to container walls. The accurate determination of trace metals in precipitation at the nanogram level requires: 1) the use of specific collection materials, 2) exacting cleaning of materials prior to use, 3) careful sample handling, 4) sample acidification for preservation, 5) very careful or Clean-Lab analysis techniques, and 6) exacting QA/QC protocols. The use of Teflon® is recommended for most trace metals. Low density polyethylene (virgin LDPE polymerized directly from ethylene gas) is a low cost alternative for most trace metals because its porous surface can be easily leached to remove adsorbed metals. High density clear polyethylene (Rubbermaid® No. 2618) is currently being satisfactorily used in the University of Delaware studies. Ultra-high purity HCl or HNO_3 and Milli-Q® equivalent water are required cleaning and preserving agents. Unfortunately the Aerochem Metric white bucket is not "virgin" polyethylene and significantly leaches Cd, Cu, and especially Zn. At the same time, it absorbs half the Pb in rain water. Automatic operation of the Aerochem Metric sampler (with an HDPE bucket) gives comparable concentrations to manual operation suggesting that between-event contamination does not occur. (See Scudlark et al.)

Preliminary analyses of an NADP/NTN trace metals network at three locations are reported (Vermette, et al.). The modification of the Aerochem Metrics sampler to incorporate all Teflon® surfaces and the use of an inductively coupled plasma mass spectrometer (ICP-MS) for analysis is well adapted to the routine analysis of As, Cd, Cu, Mn, Pb,and Zn at the ng L^{-1} level. However, Teflon® adsorbs more than 90% of the Hg in precipitation samples if not properly "pretreated" and "conditioned". Pre-baked borosilicate glass in combination with cold vapor atomic florescence spectroscopy (CVAFS) analysis is best adapted for the routine analysis of Hg in precipitation at the ng L^{-1} level. Analysis of field and laboratory quality assurance blanks and inter-laboratory comparisons, suggests that careful field handling, and careful lab procedures can produce analyses equal to Clean-Lab, and clean-dressed operator procedures (Vermette et al.).

IMPACTS ON PLANTS AND FISH

SOIL MEDIATION

Low-level accumulation of trace metals in soils causes subtle, and potentially more far reaching problems than direct smelter impacts; these include 1) uptake by plants and movement in the food chain, 2) disappearance of metal-intolerant species, and 3) overall reduction in plant growth. Trace metals in soils are made unavailable to plants via precipitation as metal carbonates, phosphates, sulfides, and silicates; and by complexation with organic matter and hydrous oxides of Fe, Al, and Mn. The thermodynamics of soil solutions favor the precipitation and complexation of trace metals, particularly in soils high in clays and organic matter. Although this capacity is large, continuous trace metal accumulation yields immobilized forms that are

increasingly more soluble and more available to plants. Acid soils and well oxidized soils increase the availability of most trace metals to plants.

Subtle impacts on plant growth may be indirect. The toxicity of trace metals to mycorrhizal fungi may reduce mycorrhizal activity, and suppress root colonization. In turn, these can lead to plant nutrient deficiency, root disease and drought stress. It is clear that host plant response to metals in soils is closely related to fungal tolerance. Dosskey and Adriano's review of soil/metal interaction, and their application of Bradley, et al.'s (1981) hypothesis of fungal mediation suggests that plants which form ectomycorrhizae with large hyphal masses outside the root surface may be capable of sustaining greater metal inputs before experiencing adverse impacts than those forming vesicular-arbuscular (VA) mycorrhizae with hyphae inside the root. Thus VA mycorrhizae-forming herbaceous plants (e.g. beans) and deciduous trees would be more sensitive to metal contamination of soil than conifers with their more tolerant ectomycorrhizae. Net sensitivity to plants is the result of soil physical and chemical properties, trace metal load, and mycorrhizal ecology. These factors cause great spatial variation in plant stress from trace metals (See Dosskey and Adriano).

MERCURY IN LAKE WATER AND FISH

Almost all atmospheric Hg is elemental Hg^{o}. In precipitation and lake water it occurs at nanogram L^{-1} (one billionth of a gram per liter) concentrations. Thus, as with the earlier analyses of trace metals in precipitation, lake water concentrations determined prior to 1980 are grossly contaminated. Blank concentrations of 0.5 ng L^{-1} must be determined in order to measure ambient levels of 1-3 ng L^{-1}. Roughly 6 billion grams of Hg circulate through the atmosphere each year. Mercury is important because the most toxic form, methyl-Hg accumulates in fish tissue at 10^{6} to 10^{7} times ambient levels . Birds, humans, and mammals that consume aquatic organisms with high Hg concentrations may incur increased risks to health (See Porcella, et al.).

An investigation of Hg cycling in northcentral Wisconsin lakes demonstrates the importance of atmospheric Hg to the geochemical cycling and bioaccumulation of Hg in temperate seepage lakes and the potential linkage between modest increases in atmospheric Hg loading and enhanced Hg levels in biota. The Hg speciation data suggest that atmospheric deposition of methyl-Hg is very small. Instead, the bioaccumulation of methyl-Hg in fish is directly related to the in-lake Hg(II) substrate available for methylation. Some elemental Hg (Hg^{o}) escapes to the atmosphere, particularly in acid waters. The Hg(II) substrate consists of labile inorganic associations (e.g. Hg^{2+} ; $Hg(OH)^{2}$), organic associations (e.g. simple amino acid Hg complexes), and labile particulate Hg complexes. The annual accumulation of methyl-Hg in fish tissue (0.15 g in Little Rock Lake) is < 10% of the annual net input of elemental Hg^{o}, yet this constant input maintains the Hg(II) substrate available for methylation. (See Fitzgerald, et al.). The concentration of methyl-Hg in fish tissue has resulted in state advisories against eating fish in thousands of lakes in Minnesota, Wisconsin, Michigan, Illinois, New York, and Florida, as well as many of the eastern provinces in Canada.

METAL TOXICITY TO FISH

There is a well-documented response of fish to trace metal toxicity. This has been developed primarily by studies of gross anatomical abnormalities in fish found in streams, estuaries, and bays receiving trace metals from point sources. The early life stages of fish are the most sensitive to trace metal toxicity. Responses of fish embryos and larvae to trace metals include death, development of teratogenic abnormalities, slowed motility and egg development, reduced or inhibited enzyme activity, and reduced growth. Specific mechanisms of fish toxicity include failure of the skeletal system to develop fully (curved, or no spine), stunting, circulatory stasis (failure of the heart tube to bend and edema of the pericardial cavity), and failure of the optic system to develop fully. It is not the developmental arrest itself but the continuous exposure to a teratogen at that critical life stage that causes the anomalies once development resumes. Aqueous metal concentrations that elicit these responses are relatively high compared to concentrations in precipitation, and various fish species respond at different levels (Weis and Weis).

Salmonids are most sensitive to elevated metal concentrations. Developmental toxicity from Zn begins at 1,400,000 ng L^{-1} for brook trout, at 500,000 ng L^{-1} of Cu for northern pike, at 250,000 ng L^{-1} of As for rainbow embryos, and at 37,000 ng L^{-1} of Cu for rainbow trout. Selenium causes mortality in rainbow trout embryos at 10,000 ng L^{-1}, and Cd concentrations of 10,000 ng L^{-1} cause cardiac malformations in rainbow trout. Hg concentrations of 1,000 ng L^{-1} cause weight loss in salmonid embryos. Adult rainbow trout exposed to water with as little as 200 ng L^{-1} of Hg and subsequently placed in clean water, produce larvae with only half the 4-day survival as larvae from non-exposed adults. Those larvae that survive have many abnormalities. For adult trout themselves, exposure to 200 ng L^{-1} of Hg significantly reduces reproductive success, increases mortality and the occurrence of abnormalities (Weis and Weis).

In contrast to these toxic metal concentrations in lake, stream or esturary water, only Hg approaches direct toxic levels in precipitation. The higher concentrations of trace metals found in precipitation are estimated from Nriagu (p. 18), or the original work of Vermette et al.. They are associated with urban precipitation, and are given below as about 3X average concentrations (This is often equivalent to the mean plus two standard deviations).

Element	As	Cd	Cu	Mn	Pb	Zn	Hg
ng L^{-1}	5000	5500	9000	35000	18000	25000	200

In mammalian teratology, a field much more intensively studied than fish teratology, it has become clear that functional deficiencies are a more subtle response to toxicants than the production of gross anatomical abnormalities. It is likely that exposure of fish embryos to low concentrations of trace metals also results in (difficult to measure) abnormal behavior in anatomically normal individuals after their birth (Weis and Weis).

CONCLUSIONS

Trace metal concentrations in the atmosphere and in precipitation have been above background levels for some 400 years. Increases above background became pronounced from 1850 to 1950 and acute from 1950 to the early 1970's. Decreases in trace metals in wet deposition have occurred since enactment and implementation of the Clean Air Act of 1970, with an annual decrease averaging 6 % over the Great Lakes. Decreases in Pb have been most dramatic approaching a total 33% reduction in parts of the northeastern United States as seen in some lake sediment cores. However, precipitation measures of Pb loading to the Great Lakes show annual decreases of 3% over L. Huron, 4% over L. Erie, and 9% over L. Ontario. In contrast, Pb deposition over Lake Superior has increased 2%annually from 1981 to 1988. The 1990 Clean Air Act amendments expands the focus of air pollution monitoring and standards from urban areas to rural areas and includes trace metals as a major item. It further extends our national concern for air pollution from impacts on human health to include impacts on ecosystem integrity, fish, and plant health.

The measurement of trace metals in precipitation, aerosols, and lake and stream waters has been seriously compromised by contamination, such that analyses prior to 1980 ehibit large positive biases. New sampling and analysis techniques developed and refined over the last 12 years have made the analysis of trace metals in all ecosystem components accurate at the microgram L^{-1} and nanogram L^{-1} levels, and, for some metals, even the sub-ng L^{-1} level. It is demonstrated that trace metal accumulation in rural ecosystems parallels the deposition of sulfur in those ecosystems. Long range transport of trace metals from fossil fuel energy production, metal mining and refining, and waste incineration dominates the geochemical cycle of trace metals in the atmosphere by factors of 2 to 28 times natural sources.

Soils are generally well-adapted to the sequestering of trace metals in both inorganic and organic precipitates, and plants can be protected from high levels of trace metals in soils by sequestering trace metals in the hyphae of fungal mycorrhizae. Spatial variation in soils that support plants impacted by trace metals is likely to be high. Soils susceptible to acidification by sulfur and nitrogen loading (low base saturation, low organic matter, coarse fractions, well oxidized, and low pH) are also likely to have plants with a low tolerance to metal toxicity. Thus the occurrence of serious trace metal impacts on plants is not likely to exceed more than 5 to 10 % of the landscape.

Lake waters can pass atmospheric Hg° to lake sediments (but availability to the water column may increase under conditions of frequent change between aerobic and anaerobic states). Reactive Hg (HgII) in lake water provides a substrate for methylation. Virtually all of the methyl Hg produced accumulates in fish tissue reaching concentrations high enough to invoke fish-eating advisories for thousands of lakes. Toxicity of trace metals to fish at critical life stages is well documented for physical abnormalities. The concentration of trace metals in precipitation is not generally great enough to directly elicit physical abnormalities in fish with the exception of the higher concentrations of Hg found in urban precipitation. Just as our ability to measure

small concentrations of metals accurately has dramatically improved, our ability to measure behavioral disabilities rather than gross physical abnormalities is also improving and will likely provide greater insight to trace metal and fish health interactions.

The study of trace metal ecology is both miniscule and immense. The concentration levels are extremely small, yet we now realize that biogeochemical cycling at the ng L^{-1} level operates just as precisely as plant nutrient cycling at the mg L^{-1} level. In the United States, the longest record of atmospheric deposition of trace metals is limited to shoreline stations at the mid-Atlantic coast and around the Great Lakes. Yet we now know that trace metal deposition is tied to fossil fuel combustion, waste incineration, metal mining, and metal refining and processing. The spatial, and temporal distribution of trace metals in atmospheric deposition is information that an environmentally concerned society should have. It is information that NADP/NTN is well suited to provide at a reasonable cost.

ACKNOWLEDGEMENTS

We and the members of NADP/NTN are indebted to the symposium authors for their willingness to share a decade of rigorous research and monitoring experience. We also thank V. Bowersox, C. Simmons, and L. Ohmann for helpful reviews of this summary.

WORDWIDE CONTAMINATION OF THE ATMOSPHERE WITH TOXIC METALS

Jerome O. Nriagu[1]

ABSTRACT.--The contamination of the atmosphere with toxic metals from industrial sources has become a global phenomenon. The cumulative emissions of Pb, Zn, Cu, Ni and Cd have been estimated to be 23, 17, 2.6, 1.3 and 0.38 million metric tonnes respectively. Industrial inputs now dominate the natural biogeochemical cycle of trace metals in the atmosphere and many other receiving ecosystems. Two opposing trends have recently become evident in the anthropogenic generation of toxic metals: the developing countries where the emissions are still rising sharply and the developed countries with a downward trend in both emissions and ambient environmental concentrations. Unfortunately, most of the available databases on trace metals in rainfall are compromised by severe sample contamination and only yield confusing insights on the human influence on the atmospheric trace metal cycle.

INTRODUCTION

The atmosphere is a key medium in the dispersal of anthropogenic generated metals and as such plays an important role in the global contamination of environmental compartments with toxic metals. It now represents the dominant pathway by which trace elements get into many ecosystems, such as the oceans and the Great Lakes (Gatz et al. 1989, Patterson and Duce 1991). The identification of the sources of atmospheric metal pollution and the determination of their emission rates are essential steps in any program aimed at controlling or reducing the levels of toxic metals in the environment. Proper inventory of atmospheric emissions are also basic to our understanding of the global biogeochemical cycles of the trace metals and in assessing the impacts of human activities on such cycles. Furthermore, the emission of toxic metals is closely linked to the most controversial air quality issue of recent years. Trace metals and S are often derived from the same industrial sources and, to some extent, the rains owe their toxicity to their trace metal burden. And the anthropogenerated metals often catalyze the oxidation of SO_2 to sulfuric acid. Thus, the human influence on the atmospheric metal cycle thus is of considerable interest because of the causal relationships that exist between the emissions of trace metals and (i) the concentrations and effects of trace metals in ambient air, (ii) the toxicity of rainfall, (iii) the deposition of toxic metals into fragile ecosystems and their effects on sensitive fauna and

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flora as exemplified by forest decline. This reports examines the perturbation of the global atmospheric cycle of trace metals by emissions from natural and industrial sources.

HISTORICAL

Contamination of the environment with toxic metals is an old human pursuit. Before the Industrial Revolution, mining and smelting operations represented the major source of trace metals in the environment, and the available records leave no doubt as to the severity of pollution in some of the classical mining regions. Xenophon (Book 3, Verse 6), for example, noted that the district around the famous ancient silver mines of Laurion (in Greece) was too contaminated [unhealthy] to warrant a visit by Ariston's son, Glaucon. The ancient Greek poet Lucretius (*De rerum natura*, Book VI) was particularly concerned about the health effects of the noxious emissions from precious metal mines:

> **And when there is mining for veins of gold and silver**
> **Which men will dig for deep down in the earth**
> **What stenches arise, as at Scaptensula!**
> **How deadly are the exhalations of gold mines!**
> **You can see the ill effects in the miners' complexions.**
> **All these exhalations come from the earth**
> **And are breathed forth into the open light of day.**

Vitruvius (Bk 8, verse 3) spoke about extensive water pollution around mines, while Pliny (Bk 33, verse 31) noted that emissions from mines and smelters were dangerous to all animals and especially to dogs. Del Mar (1880) maintained that the concern for environmental quality was as important as the social and economic factors in the interdiction of mining operations near ancient cities, a perfect example being the Roman edict forbidding any mining activities in Italy. Will Durant shared the same sentiments and in his highly acclaimed work, *The Story of Civilizations*, aptly observed that "Laurion pays the price of wealth it produces, as mining always pays the price for metal industry; plants and men wither and die from furnace fumes, and the vicinity of the works becomes a scene of desolation".

In ancient times, the dispersion of trace metals from polluting sources was local, or at most regional, in scope. The mine workings were done on a small scale but the uncontrolled smelting in open fires often resulted in severe local contamination (as noted above). Evidence of pollution in ancient times comes from the trace metal profiles of peats in the mining district of Giordano Valley near Bristol which show elevated concentrations suggesting that the Roman smelting operations produced measurable flux of pollutants to the local environment (Livett 1988). Elevated Pb concentrations in the Featherbed Moss also attest to the environmental impacts of Roman exploitation of the Derbyshire Pb deposits (Lee and Tallis 1973).

During the 16th Century, the development of large furnaces equipped with tall stacks (see Agricola 1555) forever changed the sphere of influence of the smelters. Increased trace metal deposition dating back to the Middle Ages which has been recorded in peat profiles at Gordano Valley, Featherbed Moss, Glenshieldaig (northwest Scotland) and in Lake Windermere sediment

suggests that emissions from smelters in Britain were already affecting the regional environment (Livett 1988). Furthermore, the profiles of trace metals in peat at Dravel Mose, Denmark, the ice cores from Jatunheimen Mountains, southern Norway, and lake sediments from southern parts of Norway and Finland (Livett 1988, Verta et al. 1989) all point to the fact that by the middle of the 17th century, the pollutant trace metals released from industries in Britain and central Europe were reaching the most remote regions of Scandinavia. In their study of ice cores from Greenland, Murozumi et al. (1969) also found that accelerated deposition of Pb from anthropogenic sources began in the middle of the 18th Century.

The health effects of high levels of toxic metals in the air were of some concern even during the Middle Ages. In his 1661 tract entitled Fumifium, John Evelyn condemned air pollution from coal combustion:

> **"New Castle cole, as an expert Physician affirms, causeth consumptions, phthisicks, and indisposition of the lungs, not only by the suffocating abundance of smoke, but also by its virulency: for all subterrany fuel hath a kind of virulent or arsenical vapor rising from it" (cited in Lenihan 1988, p.123).**

In John Evelyn's days, As was synonymous with poison, and his perception of the dangers of toxic metal pollution from coal combustion was remarkable.

Analyses of recent layers of peat, ice and aquatic sediments have provided historical records, dating back to the early 1800s, of ubiquitous trace metal pollution of increasing severity especially in the northern hemisphere (see MARC 1985, Levitt 1988). Since the middle of the last century, the production and discharge of trace metals in the environment have been increasing almost at a logarithmic scale (Nriagu 1979). It has been estimated that between 1850 and 1900, the worldwide industrial emissions of Cd, Cu, Pb, Ni and Zn to the atmosphere averaged about 380, 1800, 22000, 240 and 17000 tonnes respectively (Nriagu 1979). Between 1900 and 1980, the industrial emission rates for Cd, Cu, Pb, Ni and Zn increased by 8-, 6-, 9-, 51-, and 8-fold respectively (Table 1). Between 1980 and 1990, there was a 20% decline in rates of industrial emissions (compared to those of the preceeding decade) due to legislative initiatives and pollution control in the developed countries. The cumulative all-time emissions from industrial sources have been estimated to be 0.37, 2.6, 23, 1.3 and 17 million metric tonnes for Cd, Cu, Pb, Ni and Zn (Table 1). The quantities of the anthropogenerated metals clearly dwarfs the reservoirs of the trace elements in the atmosphere and many other target ecosystems and leave no doubt that mankind has become a key agent in the global redistribution of toxic metals. The short lifetime of pollutant metals in the atmosphere ensures that there is no inexorable build-up of toxic metals in the atmosphere. Nevertheless, the pervasive nature of trace metal pollution in the atmosphere is well documented in a large number of published reports (for instance, see Nriagu and Davidson 1986).

Table 1.--Historical changes in the emissions of trace metals to the atmosphere. Units: x 10^6 kg (from Nriagu, 1979).

Period	Cd	Cu	Pb	Ni	Zn
Pre-1850	63	319	2420	-	2804
1850-1900	19	92	1100	12	841
1901-1910	9	53	471	8	392
1911-1920	11	80	493	21	493
1921-1930	14	96	1120	21	622
1931-1940	17	116	1693	49	746
1941-1950	22	169	1672	80	959
1951-1960	34	230	2694	140	1514
1961-1970	54	435	3704	257	2372
1971-1980	74	585	4265	415	3252
1981-1990	59	468	3412	332	2602
TOTAL	376	2643	22990	1335	16597

GLOBAL EMISSIONS OF TRACE METALS INTO THE ATMOSPHERE

The following discussions are based on global inventories of emissions of trace metals from natural and anthropogenic sources that have recently been published (Nriagu and Pacyna 1988, Nriagu 1989). The data lead to the sgestion that mankind has destabilized the steady-state (pretechnological) atmospheric cycles of the trace metals and that the various components of the biosphere are gaining large quantities of toxic metals via the aerial route.

The summary of annual emissions from natural sources (Table 2) shows that volatile and particulate material derived from biogenic processes account for over 50% of the Se and Hg and for about 30% of the As that would have been released in prehistoric times. Volcanoes and fumaroles account for over 40% of the Cd, Hg and Ni and for 20-40% of the As, Cr, Cu, Pb, Sb, V and Zn released naturally. Volcanic eruptions are episodic in nature and the values listed should be regarded as the average source strengths. Spikes of elevated metal concentrations have been reported in the polar ice layers which can be related to major volcanic eruptions (Boutron et al. 1984). Soil-derived dusts are responsible for over 60% of the Cr, Co and Mn, for about 40% of the Mo and Zn and for 20-40% of the As, Cu, Pb and Sb emitted to the atmosphere from

natural sources. Forest fires and seasalt sprays represent minor sources of airborne trace metals, each source representing <10% of the global baseline flux (Table 2). It should be noted that the data in Table 2 over-represent the natural fluxes into the pre-industrial atmosphere since anthropogenerated metals are now being mobilized by the natural processes.

Table 2.--Emissions of trace metals from natural sources to the atmosphere ($x10^6$ kg yr^{-1}; from Nriagu 1989).

Element	Soil-derived dust	Seasalt sprays	Volcanoes	Forest fires	Biogenic sources	TOTAL
As	2.6	1.7	3.8	0.19	3.9	12
Cd	0.21	0.06	0.82	0.11	0.24	1.4
Cr	27	0.07	15	0.09	1.1	43
Co	4.1	0.07	0.96	0.31	0.66	6.1
Cu	8.0	3.6	9.4	3.8	3.3	28
Hg	0.05	0.02	1.0	0.02	1.4	2.5
Mn	221	0.86	42	23	30	317
Mo	1.3	0.22	0.40	0.57	0.54	3.0
Ni	11	1.3	14	2.3	0.73	29
Pb	3.9	1.4	3.3	1.9	1.7	12
Sb	0.78	0.56	0.71	0.22	0.29	2.6
Se	0.18	0.55	0.95	0.26	8.4	10
V	16	3.1	5.6	1.8	1.2	45
Zn	19	0.44	9.6	7.6	8.1	45

Most industrial processes release one trace metal or the other into atmosphere. The three principal contributors to worldwide trace metal pollution, however, are the burning of fossil fuels, the pyrotechnical recovery of metals from their ores and the production and use of metallic commercial products (Table 3). The burning of fossil fuels to generate energy is the dominant source of atmospheric V (98%), Ni (81%), Hg (64%) and Se (60%). Most of the V is released from the burning of fuel oil and the Mn/V ratios have been used with success for identifying air parcels from this particular source (Rahn and Lowenthal 1984). The ratios of the concentrations of Ni to metals can also be used to fingerprint any air masses released from coal-fired power

plants while Se would not be a prefered choice for normalizing other metals in atmosheric source apportionment.

The mining and smelting of base metals represent the principal industrial sources of airborne Cd (71%), Cu (66%), As (63%), Cr (55%), and Zn (54%) (see Table 3). Since As, Cd, Sb and Se are by-products in the beneficiation of base metal ores, they are often allowed to go into the "smoke" unless the concentrations are high enoh to warrant their economic recovery. This method of getting rid of unwanted accessory metals in the smelted ores is environmentally ill-advised and should be discouraged especially in the developing countries.

The automobile remains the single largest source of lead in the atmosphere, accounting for about 75% of the total Pb emission (Table 3). The contribution from this source is declining rapidly, however, in response to the reduced use of lead additives in gasoline in North America and Europe (Nriagu 1990). Secondary non-ferrous metal plants represent the principal source of

Table 3.--Worldwide emissions of trace metals from industrial sources. Units: $x10^6$ kg yr^{-1} (from Nriagu and Pacyna 1988).

Process	As	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Sb	Se	Sn	V	Zn	Ti
Energy Production	2.2	.79	13.	8.0	2.3	12.	42.	13.	1.3	3.8	3.3	84.	17.	1.1
Mining	.06	-	-	.42	-	.62	.80	2.6	.10	.16	-	-	.46	-
Smelting and Refining	12.	5.4	-	23.	.13	2.6	4.0	46.	1.4	2.2	1.1	.06	72.	-
Manufacturing Processes	-	.60	17.	2.0	-	15.	4.5	16.	-	-	-	.74	33.	4.0
Commercial Applications	2.0	-	-	-	-	-	-	4.5	-	-	-	-	3.2	-
Waste Incineration	.31	.75	.84	1.6	1.2	8.3	.35	2.4	.67	.11	.81	1.2	5.9	-
Transportation	-	-	-	-	-	-	-	248	-	-	-	-	-	-
TOTAL	19.	7.6	3.1	35.	3.6	38.	52.	332	3.5	6.3	5.1	86.	132	5.1

atmospheric Mn pollution while the iron and steel mills account for about 55% of the anthropogenerated chromium (Table 3). Refuse incineration is currently responsible for over 30% of the Hg and for 10-20% of the Cd, Sb, Mn and Sn from industrial sources. The contribution from this source is expected to rise in future as incineration becomes increasing attractive as a strategy for municipal waste management. Burning of fuel wood and agricultural wastes is the major source of trace metals in villages and remote areas of the developing countries (Nriagu 1991).

Two divergent trends have become evident in the emissions to toxic metals in the environment. As a result of pollution control measures, the discharge of metals by industries has been curtailed and the concentrations of toxic metals in the ambient environment of many developed countries

are now declining. The reduction in atmospheric metal burden is nicely demonstrated by the the Pb, Zn and Cd concentrations in the Greenland ice layers which have declined by factors of 7.5, 2.5 and 2.5 respectively since the late 1960s (Boutron et al. 1991). By contrast, the emissions of toxic metals in the developing countries continues to rise sharply (Nriagu 1991). In fact, the highest ambient concentrations of many toxic metals in the environment are now being reported in the developing countries.

PERTURBATION OF THE ATMOSPHERIC METAL CYCLE

From the inventories in Tables 2 and 3, the ratios of anthropogenic to natural fluxes of trace metals to the atmosphere have been estimated to be 28 for Pb, 5.4 for Cd, 2.9 for Zn, 3.1 for V, 1.6 for As, 1.4 for Hg, 1.8 for Ni, 1.3 for Sb, 1.2 for Cu, 0.72 for Cr, 0.63 for Se and 0.12 for Mn. Thus, with the exception of Mn, the fluxes from industrial sources either exceed or are comparable to the emissions from natural sources implying that mankind has become the key element in the global and regional atmospheric cycling of the trace elements. Numerous field studies demonstrate causal relationships between emissions and ambient concentrations of trace metals in air in many parts of the world, thereby confirming the over-riding importance of anthropogenic inputs on the regional and global atmospheric fluxes of the trace elements (see Nriagu and Davidson 1986). For instance, the atmospheric concentrations of Pb, Cd, Cu and Fe in urban areas typically fall in the range of 100-500, 1.0-5.0, 10-60, and 50-400 ng m-3 (see Nriagu and Davidson 1986). These values are well over 1000-fold higher than the concentrations in the Antarctic Peninsula (Table 4), and large fractions of the aerosols in the Antarctica come from industrial sources (Boutron and Patterson 1987, Suttie and Wolff 1991). The long-range atmospheric transport of metal pollution is shown dramatically by the high concentrations of toxic metals in the Arctic winter haze (Table 4) which can cover up to 8% of the surface area of the earth.

Most of the industries are located in the northern hemisphere and the pertubation of the trace metal cycles in this region should be more profound. The big difference in the levels of trace metals in the Arctic and Antarctic regions is noted in Table 4. Regional differences in the anthropogeneration of trace metals are also well documented in the deposition of metals into the seas and oceans (Table 5). For most of the metals, the average atmospheric fallout follows the pattern: N. Atlantic>N. Indian>N. Pacific>S. Atlantic>S. Indian>S. Pacific. This sequence is closely related to the intensities of trace metal emissions in different regions of the world. The fact that most of the emissions currently occur in the Northern Hemisphere is clearly highlighted. The maximum disparity in metal fluxes is between the North Atlantic (most polluted) and the South Pacific (least polluted); the differences in the deposition rates between the two oceans is over 50-fold for most metals (Table 5). A recent study shows that atmospheric fallout of Pb exceeds 1000 $\mu g\ m^{-2}yr^{-1}$ of the coasts of Western Europe, eastern North America, West Africa and around Japan (GESAMP 1989); these high deposition areas are adjacent to countries where the use of Pb is very intensive. The fluxes of metal pollution into the seas in Europe make the deposition rates into the oceans look small however (Table 5).

Table 4.--Atmospheric trace metal concentrations (pg m^{-3}) in the polar regions

Element	Antarctic Penninsula 1984-1985[1]	Kap Tobin,Greenland[2] March 1979-80	Kap Tobin,Greenland[2] March 1979-80
Pb	4.7	370	3210
Cu	1.0	70	500
Zn	6.1	350	37900
Cd	0.06	-	0.11[3]

[1] Dick, 1991; [2] Heidam, 1986; [3] Spitsbergen, Dec. 1973-Mar. 1974, Wiersma and Davidson, 1986.

As to be expected, industrial emissions have drastically changed the concentrations of trace elements in the rainfall. The average concentrations of trace metals in rainfall can be estimated by assuming that 70% of the natural plus anthropogenic emissions to the atmosphere (Tables 2 and 3) are deposited on the terrestrial environment, and that the volume of rainfall on land is $1.1x10^{17}$ liters (Berner and Berner 1987). It has also been assumed that rainfall accounts for 60% of the total atmopsheric fallout. The calculated average concentrations of the trace elements in wet precipitation are shown in Table 6. It would seem reasonable that the calculated concentrations fall between the values observed in rural and remote locations. A notable feature in Table 3 is that the concentrations of trace metals in some urban areas now exceed the levels considered unsafe in drinking water and shown to be injurious to some aquatic organisms. This should be a matter of some concern in developing countries where rain water is consumed by a large number of people in the urban areas.

The average concentrations of trace metals in rainwater shown in Table 6 are much lower than those one typically finds in the literature (see Galloway et al. 1982 for good compilation). The lower concentrations are more consistent with (a) the emission inventories in Tables 2 and 3, and (b) the low ambient air concentrations of trace metals in rural and remote areas (for instance, see Wiersma and Davidson 1986, Patterson and Duce 1991). The low concentrations implies that the rainwater samples are highly prone to being contaminated during collection, treatment and analysis. Few laboratories that monitor the chemistry of atmospheric deposition employ ultra-clean laboratory techniques or have the capability for measuring trace metal concentrations in the ng l^{-1} range. Most of the available databases on trace metal concentrations in rainfall are compromised by severe sample contamination and thus provide veryconfusing insight on the question of atmospheric metal pollution. Our understading of the human influence on the distribution, fate and effects of toxic metals in the atmosphere has thus far been twarted by lack of credible data obtained using rigorous ultra-clean methods (see, for instance, Tramontano et al. 1987).

Table 5.--Fluxes of trace metals (μg $m^{-2}yr^{-1}$) into the seas and oceans (from GESAMP, 1989).

Ocean/Sea	As	Cd	Cu	Hg	Ni	Pb	Zn
N. Atlantic	67	36	400	7.6	291	1030	1600
S. Atlantic	5.4	2.9	31	1.8	24	80	127
N. Pacific	13	7.1	77	6.5	57	200	312
S. Pacific	1.3	0.73	7.8	3.0	6.0	20	31
N. Indian	21	12	125	4.9	97	330	514
S. Indian	2.1	1.5	17	3.7	13	50	69
North Sea	650	300	2700	-	1200	14000	14000
Black Sea	460	140	2900	-	-	2400	11000
NW Mediter.	<1000	<1000	4200	-	-	29000	34000

The levels of trace metals in rainfalls (Table 6) now exceed the dissolved concentrations in many aquatic ecosytems, and there is considerable evidence to suggest that the aerial inputs now dominate the biogeochemical cycling of the trace metals in such environments (Nriagu and Pacyna 1988). For instance, the atmospheric inputs are now several times higher than the riverine delivery of dissolve trace metals to the oceans (Table 7). Other evidence for the perturbation of the marine cycle of Pb by atmospheric inputs include (a) there is a 15-fold increase in Pb content of recent coral growth layers compared to those of a century ago; (b) the marked change in the form of Pb profiles in ocean water column reflects the strong atmospheric source intensity; (c) a 26-fold difference in the Pb concentrations in mixed surface layers has been noted between the North Atlantic (polluted) and the South Pacific (relatively unpolluted); and (d) a measurable shift in the isotopic signature of Pb in surface waters towards the isotopic ratio of airborne industrial Pb has also been reported (see Patterson and Settle 1987 for detailed discussion of oceanic Pb pollution). A recent analysis of the Atlantic Ocean sediments show a sharp increase in the Pb content of the surficial layer which has been attributed to increased influx of anthropogenic Pb (Veron et al. 1987).

Table 6.--Concentrations (ng L^{-1}) of trace metals in wet deposition

Element	Urban1[1]	Rural[1]	Remote[1]	Predicted[2]
As	900	240	10	120
Cd	350	50	4	33
Cr	1200	380	25	340
Cu	2800	450	20	270
Pb	6000	1400	80	1320
Hg	65	25	2	22
Ni	1500	500	35	330
V	2000	700	50	440
Zn	3500	800	75	705

[1]Compiled from recent literature.
[2] Predicted using the emission data in Tables 2 and 3.

Several studies have shown that aquatic ecosystems respond rather quickly to changes in anthropogenic inputs of trace metals. For example, the surface ocean waters off the northeastern United States have shown a 30-40% decline in Pb concentration due to the phase-out of leaded gasoline. The isotopic composition of Pb in the surface waters of the Great Lakes is very similar to the isotopic signature of the ambient aerosol (Flegal et al., 1989); the close correlation stems from the fact that the life-time of Pb in the epilimnion is only a few days and the Pb concentration is controlled by recent atmospheric inputs. Also, there has been a drastic shift in the isotopic composition of Pb in Lake Erie sediments which reflects the declining role of atmospherically derived automotive Pb (Mueller 1988). The installation of a tall stack at the Cu/Ni smelters in Sudbury (Ontario) has reduced the rates of accumulation of trace metals in the local lake sediments (Nriagu and Rao 1987), while the reduced consumption of leaded gasoline has engendered the recent decline in Pb accumulation in aquatic sediments which has been documented in many parts of the world (Levitt 1988).

Table 7.--Atmospheric versus riverine inputs of trace metals into the oceans

Element	Dissolved in Rivers ($ng\ L^{-1}$) [1]	River Input ($x10^9\ g\ yr^{-1}$) [2]	Atomospheric Input ($x10^9\ g\ yr^{-1}$) [3]
As	47	1.6	5.8
Cd	2.1	0.07	3.2
Cr	172	5.8	-
Cu	115	4.0	34
Hg	0.82	0.03	1.7
Mo	12	0.41	-
Ni	135	4.6	25
Pb	8.5	0.29	88
Sb	14	0.48	-
Se	35	1.2	-
Zn	165	5.6	136

[1] Based on published data obtained using the ultra-clean laboratory proceedures.
[2] Assuming total discharge of water by rivers to be $3.4 \times 10^{16}\ L\ yr^{-1}$.
[3] From GESAMP, 1989.

These studies clearly emphasize the strong influence of atmospheric pollution on the trace metal economy of many ecosystems and the need for emission controls as a critical means of reducing the levels and effects of toxic metals not only in the air but in our water, soils and foods as well.

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CLEAN AIR ACT REQUIREMENTS FOR TRACE METALS INFORMATION

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ABSTRACT.--The Clean Air Act Amendments of 1990 have expanded the requirements for trace metal and air toxics information in urban areas and added new requirements for this information in rural areas and ecosystems. Specific provisions germane to trace metals and other air toxics compounds are found in Title III, Section 112 and in Title IX, Section 901. In response to these provisions, the United States Environmental Protection Agency (EPA) plans to conduct research in atmospheric monitoring networks in urban areas, in the Great Lakes watershed, and in regional components of a national Clean Air Act status and trends network.

INTRODUCTION

Historically, the Clean Air Act has included requirements for the acquisition and assessment of information about trace metals and other air toxics compounds. This has resulted in research and regulatory assessment that included measurements of trace metals and associated atmospheric toxic compounds from stationary sources and the ambient air. This paper reviews the legislative framework of the Clean Air Act relevant to trace metals, discusses specific provisions of the recent 1990 Clean Air Act Amendments that are germane to trace metals and air toxics compounds, and identifies research plans for meeting these provisions.

LEGISLATIVE FRAMEWORK

The provisions for attainment and maintenance of national ambient air quality standards (Sections 108 and 109 of the Clean Air Act and subsequent Amendments) have formed the cornerstone of the national strategy to reduce and control air pollution. The fundamental concept underlying these national ambient air quality standards (NAAQS) is that they represent threshold levels of air pollution below which the best scientific evidence and judgement indicates that humans experience no adverse health effects.

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The NAAQS have been established to regulate levels of "criteria" air pollutants: particulate matter, lead, sulfur dioxide, nitrogen dioxide, ozone, and carbon monoxide. Establishing and revising these standards has required a scientific determination of the relation between ambient concentrations of these pollutants, their sources, and associated health effects. This in turn has required the deployment and operation of national monitoring networks to measure the concentrations of these pollutants and to identify their sources. The primary focus of these networks has been urban areas. However, since the NAAQS apply only to a relatively small number of air pollutants, additional legislative mechanisms were needed to establish regulations for the large number of stationary sources of trace metals and toxic emissions not covered by these standards.

Thus, Sections 107 and 110 of the Clean Air Act of 1970 provided for the establishment of metropolitan statistical areas (formerly air quality control regions), the determination through statistical analysis of whether and by how much air pollution in each region exceeds the relevant NAAQS, and the development of strategies and regulations known as State Implementation Plans (or SIP's) to achieve compliance with the NAAQS.

These SIP's typically mandated control of categories of "existing" stationary sources of air pollution and were less stringent than federal standards for categories of "new" stationary sources. Sections 111 and 112 of the 1970 Clean Air Act Amendments required EPA to promulgate New Source Performance Standards (NSPS) and National Emission Standards for Hazardous Air Pollutants (NESHAPs), respectively. Stationary source control regulations promulgated under sections 111 and 112 have been largely responsible for improvements since 1970 in ambient air quality, which have occurred for all criteria pollutants except ozone.

An additional legislative mechanism was employed for lead and other compounds emitted from motor vehicles. Ambient concentrations of this trace metal are generally attributed to mobile sources and a limited number of stationary sources. Thus, Section 211 of the 1970 Clean Air Act and subsequent Amendments has reduced tailpipe lead emissions by mandating a gradual phase-down of lead in gasoline used in motor vehicles.

In summary, prior to 1990, Clean Air Act legislation has managed the impact of air pollutants on human health through implementation of national ambient air quality standards. Determination of the relationship between ambient air quality and human health has been accomplished primarily through atmospheric measurements to characterize spatial and temporal concentrations of air pollutants in populated urban areas. Ambient air quality has been improved largely through stationary source control regulations which have required short term source emissions measurements.

RECENT REQUIREMENTS FOR TRACE METAL INFORMATION

In contrast to this historical legislative framework, the Clean Air Act Amendments of 1990 include new provisions of particular relevance to the need for trace metal and toxic compound information. Although continuing the historic focus on urban areas, the 1990 Clean Air Act expands the need for ambient air measurements beyond urban areas by mandating significant research to characterize the spatial and temporal impacts of trace metal and toxic compounds on rural ecosystems. These new legislative provisions are found in Title III, Section 112 and Title IX, Section 901 of the 1990 Clean Air Act Amendments.

In establishing new provisions for trace metals and other hazardous air pollutants in Section 112 (k), Congress determined that emissions of hazardous air pollutants from area sources may present significant risks to public health in urban areas. Area sources consist of small, unregulated stationary and mobile sources. This determination was based in part on the large number of potentially exposed individuals in urban areas as well as the risk of carcinogenic and other adverse health effects from hazardous air pollutants.

Thus, Section 112 (k)(2) requires a program to conduct research that will characterize and identify the sources of hazardous air pollutants in urban areas. To meet these objectives, the Environmental Protection Agency (in consultation with State and local air pollution control agencies) will design a program that will: (1) conduct ambient monitoring for a broad range of hazardous air pollutants (including volatile organic compounds, metals, pesticides, and products of incomplete combustion) in a representative number of urban areas; (2) characterize the sources of these compounds and determine those contributing area sources as well as their contribution to public health risks; and (3) consider factors which can elevate public health risks from these sources such as atmospheric transport and transformations.

Section 112 (k)(2) requires the development of a national strategy based on this research that would control emissions of hazardous air pollutants from area sources. The national strategy must identify at least 30 hazardous air pollutants that pose the greatest threat to public health in the largest number of urban areas; source categories which, individually or in the aggregate, present a threat of adverse effects to human or environmental health; source categories which represent 90 percent or more of the area source emissions of the 30 pollutants mentioned above; and additional research needs in monitoring, analytical and measurement methodology, modeling, or pollution control technology. A report of this national strategy is to be transmitted to Congress in 1995.

Section 112 (m) of the 1990 Clean Air Act Amendments requires EPA, in cooperation with the National Oceanic and Atmospheric Administration, to conduct a program to identify and assess the extent of atmospheric deposition of hazardous air pollutants to the Great Lakes, Chesapeake Bay, Lake Champlain, and coastal waters (hereafter, this group is referred to as the "Great Waters"). As a part of this program, EPA will conduct atmospheric measurements and monitoring of these Great Waters; investigate the sources, concentrations, and deposition rates of these pollutants; conduct research to develop and improve monitoring methods and source attribution techniques; evaluate adverse effects to public and environmental health, including

ecosystem health; and sample biota in Great Waters ecosystems and characterize the sources of any identified pollutants.

Section 112 (m) contains additional requirements that are specific to the Great Lakes. These requirements mandate the establishment and operation of a Great Lakes atmospheric monitoring network to characterize trace metals and other hazardous air pollutants and to estimate atmospheric deposition of these substances. This network is to be coordinated with the Integrated Atmospheric Deposition Network called for in the Great Lakes Water Quality Agreement between the United States and Canada. Moreover, EPA is to establish by December 31, 1991 at least one facility on each of the five Great Lakes capable of monitoring hazardous air pollutants in both wet and dry conditions. The trace metal and hazardous air pollutant information collected by both United States and Canadian participants in this monitoring network is to be comparable (from a measurement and analytic perspective) and compatible with appropriate integrated databases from both countries.

The focus of these Great Lakes provisions in Section 112 (m) is on the largely rural watershed of the lakes and on the ecosystems contained in the watershed. The measurements acquired through the monitoring network will be used to identify and track the movement of hazardous air pollutants to the lakes and to determine the portion of total loadings to the watershed attributable to the atmospheric pollution and sources. To the extent that atmospheric sources are significant, the monitoring data will be essential in developing strategies for regulations, remedial action plans, and pollution prevention.

Section 112 (n) of the 1990 Clean Air Act also requires the acquisition and assessment of trace metal and air toxics data. In contrast to the Great Lakes and Great Waters focus of the previous provisions, this requirement focuses specifically on electric utility steam generating units. Section 112 (n)(1) requires EPA to conduct a study of the hazards to public health reasonably anticipated to occur or remain as a result of utility emissions after the imposition of the various provisions of the 1990 Clean Air Act. In a separate study required under Section 112 (n)(2), EPA is to study mercury emissions from electric utility steam generating units, municipal waste combustion units, and other sources, including area sources. This study is to characterize not only the mercury emissions but also the human and environmental health impacts of these emissions.

The second group of legislative provisions that require trace metal and air toxics information is found in the Title IX, Section 901, clean air research provisions of the 1990 Clean Air Act Amendments. These provisions identify broad new environmental and ecosystem measurement and monitoring research objectives.

Sections 901 (a), (b), and (c) direct EPA to conduct a research and development program that would include research, testing, and development of methods for sampling, measurement, monitoring, analysis, and modeling of air pollutants. This program is to include the establishment of a national network to monitor, collect, and analyze data (with quantification of certainty) on the status and trends of air emissions, deposition, air quality, surface water quality, forest condition, and visibility impairment. Similar research is to be done to increase understanding of the sources of ozone precursors, formation, and transport.

Section 901 (e) directs EPA to conduct ecosystem research to improve the understanding of the short- and long-term causes, effects, and trends in damage from air pollutants. This research is to include: identification of regionally representative and critical ecosystems; characterization of the causes and effects of chronic and episodic ecosystem exposures to air pollutants; development of improved atmospheric models and monitoring systems for evaluating exposures and effects of the multiple environmental stresses associated with air pollution; and evaluation of the effects of air pollution on water quality, forests, materials, biological diversity, soils, and crops.

EPA RESEARCH PLANS

FOR HAZARDOUS AIR POLLUTANTS AND TRACE METALS

The brief review of the 1990 Clean Air Act Amendments presented above illustrates the increased importance of research to characterize hazardous air pollutants and trace metals and their human and environmental health effects in both urban and nonurban environments. Also illustrated is the significance of the new emphasis on the need for information about these air pollutants and their impacts on predominantly nonurban ecosystems. This review further indicates that the provisions of Section 901 have more ambitious environmental implications than those of Section 112 because of the number of air pollution and ecosystem research objectives included.

Currently, EPA is planning an integrated series of new and existing atmospheric and ecosystem monitoring networks designed to achieve many of these research objectives. This Clean Air Act status and trends network, operated through the Environmental Monitoring and Assessment Program (EMAP), is being designed and implemented by a team of environmental scientists that includes representatives from EPA, State air pollution control agencies, other federal agencies, corresponding Canadian federal and provincial agencies, and universities. The details of this design, which is too complex to describe in the limited context and space of this paper, will be the subject of final scientific peer review and journal publication later this year.

This atmospheric and ecosystem network will include a Great Lakes trace metals and air toxics monitoring component. Designed to achieve the Section 112 (m) schedule of establishing at least one site on each of the Great Lakes by December 31, 1991, these sites will be a part of the United States and Canadian Integrated Atmospheric Deposition Network.

A separate ambient monitoring network will be established to achieve the urban area source provisions of Section 112 (k). This urban air toxics research network, which will measure trace metals and air toxics compounds, will be a part of the Enhanced Ozone Monitoring Network required under Title I of the 1990 Clean Air Act Amendments. The current plan for this network is that one site in each of twenty five metropolitan areas that have been identified as serious, severe, or extreme ozone nonattainment areas will characterize volatile organic compounds and aldehydes. A subset of these sites will be selected for supplemental measurements of trace metals, pesticides, and other toxic compounds. Additional measurements will be made at these

sites to assist in the identification of sources contributing these air pollutants to the ambient air in the urban environment.

ANALYSIS AND DEPOSITION OF TRACE METALS IN ONTARIO

Daniel B. Orr, Michael J. Shaw and Neville W. Reid[1]

ABSTRACT.--Results of monitoring for selected trace metals in wet deposition in Ontario are presented. Spatial trends indicate a decreasing gradient from south to north, consistent with the location of the main emission sources in and to the south of the province. Anomalies in this typical deposition pattern are associated with local emission sources. Mass loadings to the Laurentian Great Lakes have been calculated. Loadings of the selected metals into the Great Lakes have decreased over time, with the exception of increased lead and manganese inputs into Lake Superior. Special studies complementing the regular monitoring program are described.

INTRODUCTION

Direct atmospheric deposition is now recognized as a significant input pathway of toxic trace metals into the Laurentian Great Lakes and their drainage basin. For instance, the International Joint Commission (1988) estimates that more than 90% of the lead entering Lakes Superior, Huron and Michigan is input from the atmosphere. The proportions estimated for other critical pollutants and the other lakes in the Great Lakes system are smaller, but are always significant.

The ramifications of trace metals deposition in the Great Lakes system are realized in more pragmatic terms. In Ontario, for example, annual consumption advisories are issued for top predator fish species based upon muscle mercury concentrations (Ontario Ministry of the Environment 1991). Similarly, an advisory warning against the consumption of moose and deer liver and kidneys is in effect because of their elevated cadmium levels (Glooshenko et al. 1988). With the exception of localized effects, no widespread phytotoxological injury to cash crops has been reported in Ontario. However, vegetable crops grown on soils in regions of high trace metals deposition and no local sources rapidly take up and assimilate these metals (Czuba and Hutchinson 1980).

This paper describes the spatial and temporal trends of selected trace metals wet-only deposition monitored by the Ontario Ministry of the Environment (OME), under the auspices of the Acidic Precipitation in Ontario Study (APIOS). The wet-only deposition trends stated in this paper update a previous report by Reid et al. (1989), by using data for the period 1981-1988. Special studies and new initiatives complementing the regular monitoring program are discussed also.

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NETWORK OPERATIONS

Trace metals wet-only deposition is monitored in Ontario in the APIOS Cumulative Network. The density of samplers is greatest in the southern part of the province, where the highest concentrations are expected. Network operations have been described by Chan et al. (1985). Briefly, an integrated precipitation sample is collected over a 28-day period, commencing every fourth Tuesday, using an M.I.C. Type A wet-only collector, fitted with a polyethylene bag insert. No preservative solution is added to the sample. The implications associated with this particular sampling scheme have been described by Chan et al. (1983) and Tang et al. (1987).

An aliquot of each cumulative precipitation sample is acidified with a 1% ultrapure nitric acid solution. The empty bag is leached for 24 hours in a 5% ultrapure nitric acid solution, then both portions are analysed for copper (Cu), nickel (Ni), lead (Pb), manganese (Mn), zinc (Zn), cadmium (Cd), iron (Fe), aluminum (Al), vanadium (V), and arsenic (As) by graphite furnace atomic absorption spectrometry.

Wet deposition is calculated directly as the product of precipitation concentration and precipitation depth. Mass loadings into the Great Lakes are calculated directly as the product of wet deposition and the respective surface areas of the lakes.

RESULTS

The spatial trends described are based upon results from thirty-three sites in operation during the study period. The temporal trends and estimates of mass loadings into the Great Lakes stated are based upon results from selected sites located within 20 km of the shoreline of the Great Lakes. Discussion of results is limited to the elements Pb, Mn, Zn and Cd.

SPATIAL TRENDS

The pattern of wet deposition for lead is presented in Figure 1. This figure shows a strongly decreasing gradient in the annual wet deposition from south to north, a pattern typical for the other pollutants considered here and for most pollutants monitored in Ontario (Tang et al. 1986). This observation is consistent with the fact that pollutant sources are mainly located in and to the south of the province. The annual wet deposition of Pb ranges from greater than 60 g ha^{-1} in the south to less than 30 g ha^{-1} in the north. For Mn the range is from greater than 45 g ha^{-1} to less than 20 g ha^{-1}. For Zn the range is from greater than 60 g ha^{-1} to less than 20 g ha^{-1}, while Cd deposition ranges from greater than 2.0 g ha^{-1} to less than 0.5 g ha^{-1}.

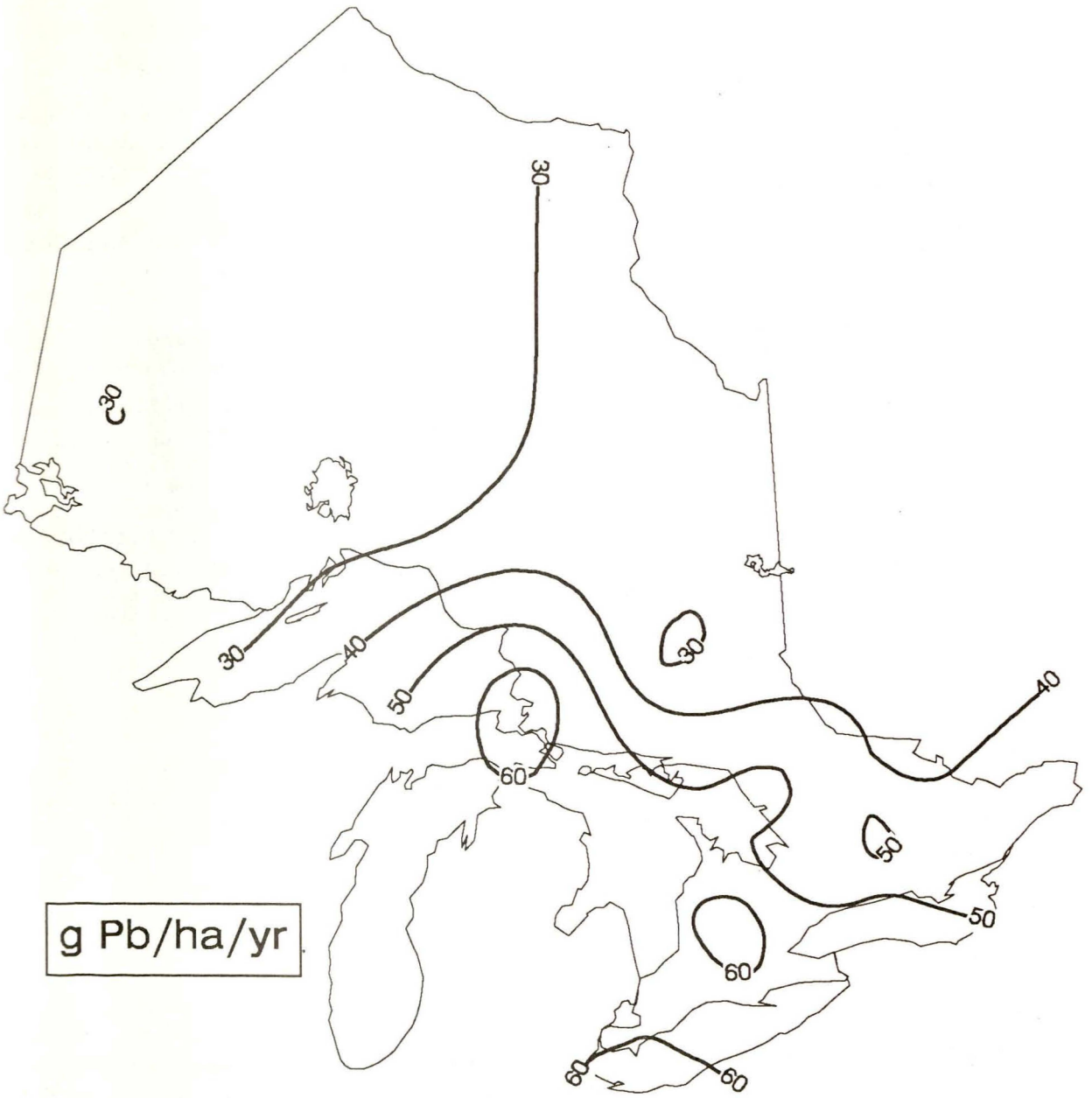

Figure 1.--Annual wet deposition (g ha^{-1}) for Pb in Ontario, 1981-1988.

Figure 1 also illustrates a deposition feature typical of the northern portion of the province. This is the occurence of localized, elevated levels of Pb, Mn, Zn and Cd. Hot spots for Mn and Pb can be readily associated with emissions from steel mills in Sault Ste. Marie and an iron-ore sintering plant in Wawa. Zinc and Cd anomalies can be attributed to emissions from the non-ferrous smelters in Sudbury.

TEMPORAL TRENDS

The temporal trend of Pb mass loading is shown in Figure 2.

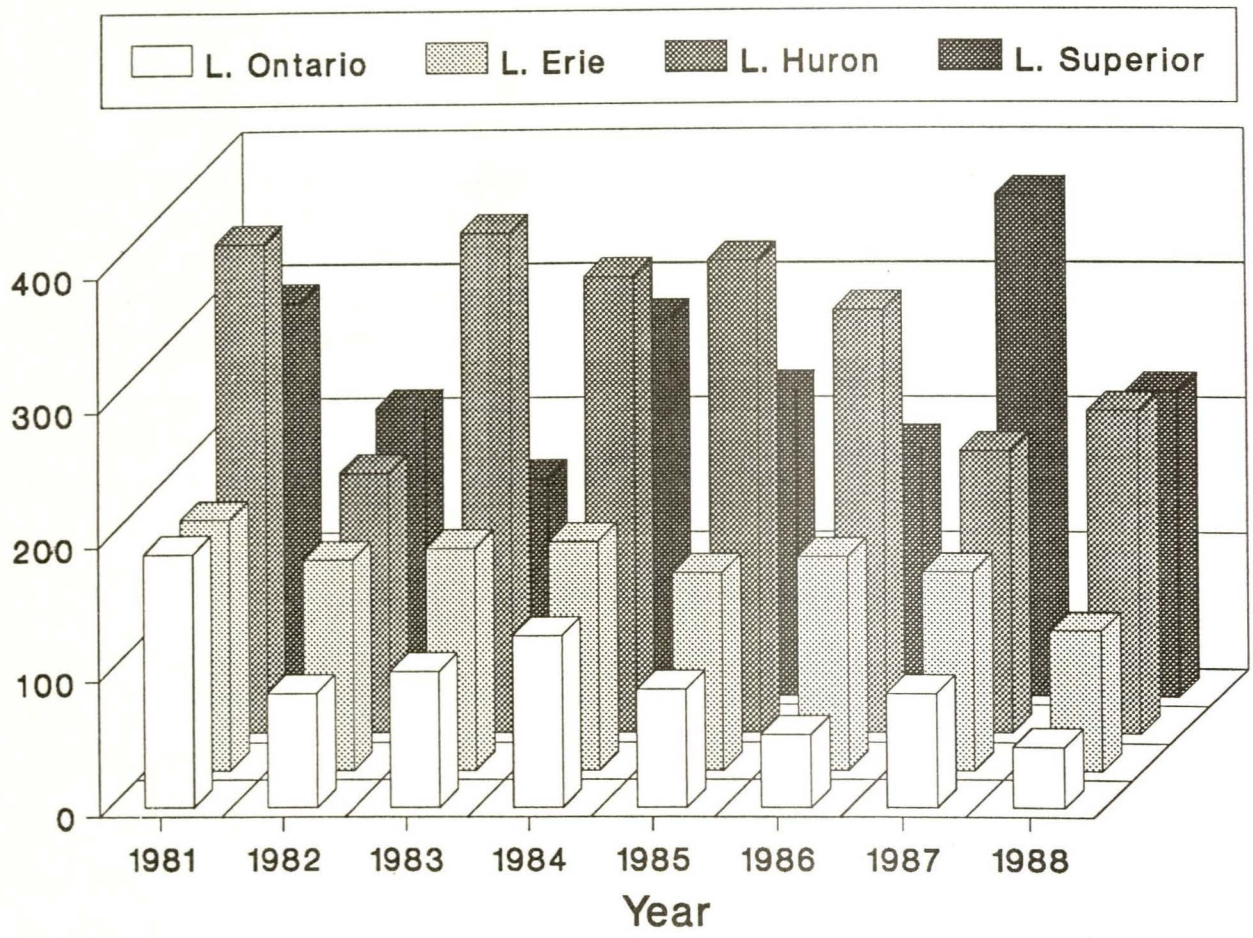

Figure 2.--Mass loading of Pb (x 10^3 kg) to the Laurentian Great Lakes, 1981-1988.

The temporal profiles for Mn, Zn and Cd loading are similar to the pattern observed for Pb, that is, there is considerable variability from year to year. It may be noted that during 1982 the non-ferrous smelting operations in Sudbury were shut down for most of the year because of a labour strike. Despite the annual variability, it is possible to discern decreasing temporal trends for each of the selected metals into the lakes using classical time series analysis (for example, Reinmuth 1977). The notable exceptions to this observation are for Pb and Mn loading into Lake Superior, where a slight increase is seen over the study period. The average mass loadings and annual per cent change for the study period are summarized in Table 1.

Table 1.--Estimated average mass loadings (x 10^3 kg) to the Laurentian Lakes, 1981-1988. The annual per cent change in temporal trend appears in parentheses.

Element	L. Ontario	L. Erie	L. Huron	L. Superior
Pb	96.3 (-8.8)	153.4 (-4.3)	296.8 (-3.3)	244.1 (+1.8)
Mn	61.0 (-0.7)	129.1 (-2.2)	167.4 (-0.9)	177.3 (+5.6)
Zn	87.5 (-10.0)	140.0 (-4.0)	220.9 (-3.7)	244.2 (-5.5)
Cd	1.5 (-6.3)	5.1 (-11.7)	4.9 (-11.3)	5.0 (-9.8)

The decreasing trend in Pb loading for several lakes is to be expected, following the phase-out of Pb in gasoline in North America. The increasing trend for Lake Superior suggests that other sources, presumably mining, dominate in this area.

SPECIAL STUDIES AND NEW INITIATIVES

ANALYTICAL MEASUREMENTS

Since September, 1990 all APIOS cumulative precipitation samples have been analysed by inductively-coupled plasma/mass spectrometry (ICP/MS). This method achieves more sensitive limits of detection and enables the determination of more exotic elemental tracers, such as In, Sb, Se, and Ge.

DAILY PRECIPITATION SAMPLING

Daily precipitation samples are collected at the APIOS Dorset event site in south-central Ontario for trace metals analysis. Samples are collected in Aerochem Metrics precipitation collectors fitted with polyethylene bag inserts. The samples are analysed by ICP/MS. Residence time analysis (Poirot and Wishinski 1986) is able to delineate the boundaries of implied source areas using this data, as shown in Figure 3.

In this example, air parcel trajectories were calculated for 1989 daily samples with high V deposition, that is, values greater than the 75th percentile. The amount of time an air parcel spent over a source area was calculated, with the results depicted as isolines of probability. Heaton et al. (1990) postulate that non-crustal V is a useful tracer for regional pollution sources, notably oil combustion. The results illustrated in Figure 3 substantiate this premise, implicating midwest sources.

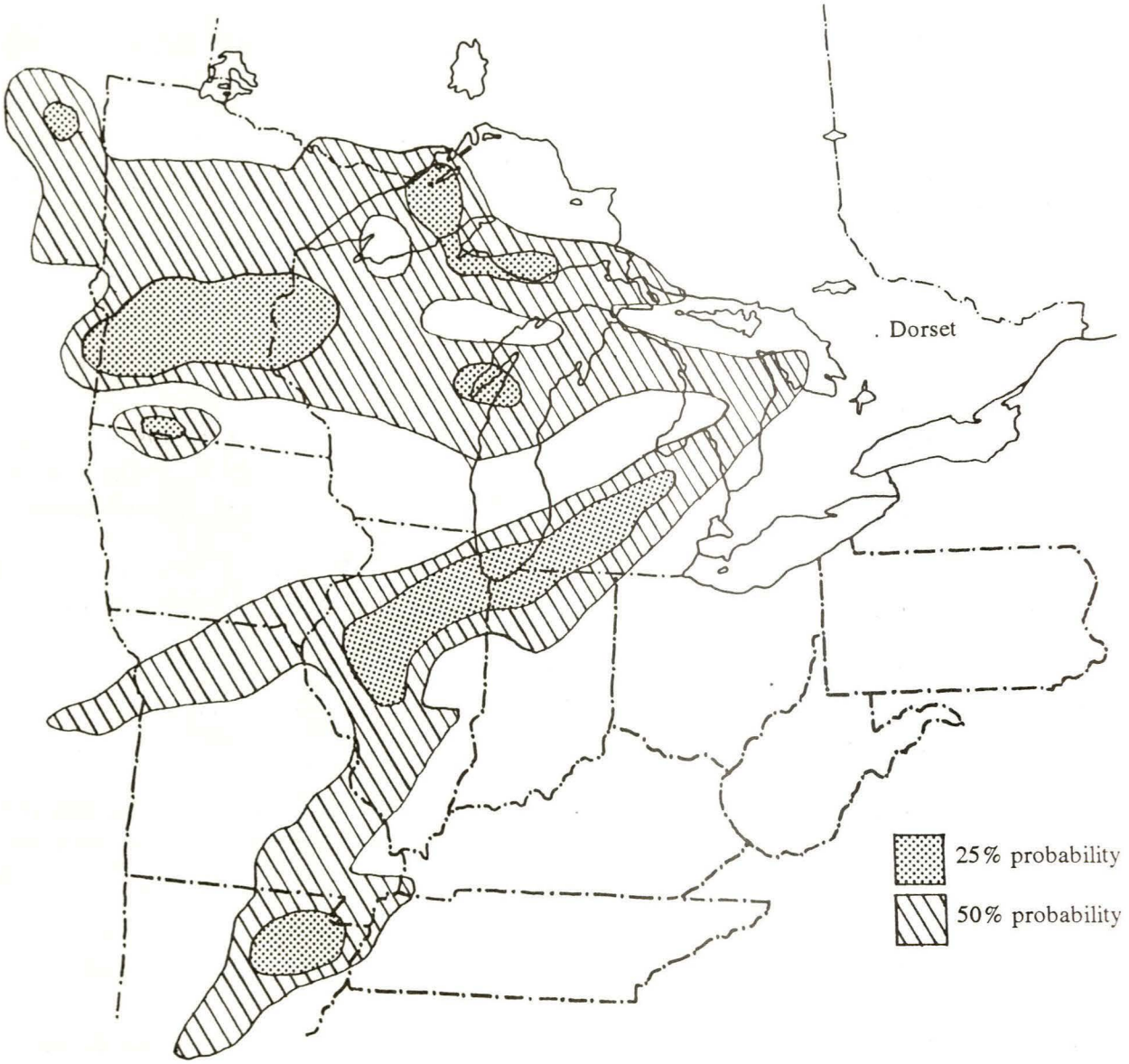

Figure 3.--Residence time analysis plot for high V deposition in daily precipitation samples collected at Dorset, Ontario.

MERCURY IN PRECIPITATION SAMPLING

Mercury concentrations in northwestern Ontario daily precipitation on the order of 1 microgram L^{-1} have been reported (Glass et al. 1986). These results are considered qualitative only because the preservative solution of 0.06% potassium dichromate and 1% nitric acid was ineffective in preventing wall losses and volatilization. Mercury in cumulative precipitation is being re-investigated, with method development focussing on the use of bromine monochloride or hydrogen peroxide as stabilizing agents, and analysis by cold vapour atomic absorption.

SUMMARY

The deposition of trace metals in Ontario generally decreases spatially from south to north. Deposition in the province and mass loadings to the Great Lakes have also generally decreased over time since 1981. The substantial trace metals deposition data base generated by routine monitoring and special studies activities has enabled the Ontario Ministry of the Environment to develop considerable expertise in the analysis and interpretation of trace metals data - a resource which other deposition monitoring agencies could draw upon when they consider trace metals for their chemical target list.

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ANALYSIS & DEPOSITION OF TRACE METALS AROUND THE GREAT LAKES

Edward W. Klappenbach[1]

ABSTRACT.--The Great Lakes Atmospheric Deposition (GLAD) network is designed to collect precipitation samples around the shoreline of the Great Lakes. Calculations of the annual volume weighted means and loadings for selected metals to each of the Great Lakes are estimated through the subsequent analysis of the wet deposition samples taken at various sites around the lakes. Both precipitation and loadings to the Great Lakes are variables. Site variations in annual precipitation amounts, especially in and around urban areas such as southern Lake Michigan and western Lake Ontario, influence the loadings to each lake. This paper examines the annual volume weighted means (VWM) of metals around the Great Lakes.

INTRODUCTION

The Great Lakes of North America collectively comprise the largest area (244,007 km^2) of fresh water on the surface of the earth as reported by Herdendorf (1982) and represent a great natural resource to both the United States and Canada. Under the Great Lakes Water Quality Agreement of 1972 these two nations developed surveillance, monitoring, and research activities to protect and reclaim, if necessary, the chemical and physical quality of the Great Lakes Basin. The importance of atmospheric deposition to these lakes was recognized in the 1970s by Shiomi and Kuntz (1973).

The problems of precipitation measurement over the Great Lakes using data from shoreline sites were addressed by Changnon and Huff (1966), Wilson (1977), and Bolsenga (1979). In 1981 the United States Environmental Protection Agency established an atmospheric deposition network consisting of thirty five (35) wet-only precipitation samplers along the shoreline of the Great Lakes. In January 1986 the size of the network was reduced from 35 sites to 20 sites because of funding reductions. The sites are located in both rural and urban locations. A rural site is any site at least 40 km from a metropolitan center of population greater than 15,000. Urban sites are all sites falling within 40 km of any metropolitan area with a population greater than 15,000.

The purpose of this network is to determine the annual volume weighted means (VWM) and loadings of metals, nutrients, and other inorganic compounds to each of the lakes. In addition,

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this monitoring program is designed to determine spatial and temporal trends in deposition, to identify emerging problems in atmospheric pollution in the Great Lakes Basin, and to provide source information for regulatory action. This report examines the metals data obtained from the Great Lakes Atmospheric Deposition (GLAD) network from 1982 through 1989. Annual loadings are calculated for these metals at each site based upon the product of the annual volume weighted means (VWM) and their annual precipitation amounts. Investigations into the loadings of metals from precipitation have been performed by Barrie et al. (1987), Eisenreich (1980), Gatz et al. (1989), Reid et al. (1989), and Ross (1987).

WET DEPOSITION SAMPLING METHODOLOGY

To obtain wet deposition concentrations of metals, the samples must be handled very carefully by each site operator and also by the chemist performing the analysis in the laboratory. The sampling period has an effect on the wet deposition of metals as indicated by de Pena et al. (1985). Investigations done by Chan et al. (1983) and Ross (1986) point out the problems encountered when collecting precipitation samples in polyethylene buckets or bags for analyses of heavy metals. As pointed out by Barrie (1988) metals may yield an aerosol signature from a region that is sufficiently distinct that its presence at a distant receptor can be distinguished from that of other source regions.

LOADINGS TO THE LAKES

As reported by Barrie (1986) the measurement of metal species concentrations were more suited to special intensive research than to routine network monitoring. However, total concentrations of many metals can be measured routinely by networks following proper sample collection, handling, and analysis procedures.

Precipitation samples are collected at the GLAD sites in polyethylene bag liners on a weekly interval (each Tuesday) provided a minimum of 500mL of precipitation (1/8 inch of water or 1 1/4 inches of snow) is in the Aerochem Metrics sampler. Both the liners and the 500mL bottles in which the precipitation samples are sent to our laboratory are checked for contaminants prior to shipment to the field site operators. All site operators are properly clothed to ensure that sample contamination is kept to a minimum. The volume of the sample is measured by the respective GLAD site operator, and then a 500mL sample is mailed to our laboratory.

Each precipitation sample is analyzed for twenty two (22) metals. They are aluminum (Al), arsenic (As), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), strontium (Sr), titanium (Ti), vanadium (V), and zinc (Zn). Seven (7) of these metals (Na, K, As, Cr, Cd, Pb, and Ni) are analyzed using atomic adsorption (AA) spectrophotometry. The other fifteen (15) metals are analyzed by inductively coupled argon plasma (ICP) spectrophotometry.

Instructions regarding the sample collection and laboratory analysis are described in the station operator's manual (1990a) for the Great Lakes National Program Office and the quality assurance project plan for the Bionetics Corporation (1990b), respectively. The limit of detection (LOD) of these metals by our contractor laboratory are given in Tables 1 and 2. The concentrations of these metals are expressed in mg L^{-1}. A report of site visits and evaluations of the GLAD sites was made by Murphy (1985). This report identified siting problems which were corrected. In some cases a change in sampler location was necessary.

Table 1.--ICP detection limits for metals in precipitation.

Metal	Detection Limits (mg L^{-1})	Range (mg L^{-1})
Al	0.02	0.020 - 2
B	0.008	0.008 - 2
Ba	0.002	0.002 - 2
Be	0.001	0.001 - 2
Ca	0.05	0.050 - 2
Co	0.0025	0.003 - 2
Cu	0.0025	0.003 - 2
Fe	0.005	0.005 - 2
Li	0.005	0.005 - 2
Mg	0.005	0.005 - 2
Mn	0.002	0.002 - 2
Sr	0.001	0.001 - 2
Ti	0.004	0.004 - 2
V	0.004	0.004 - 2
Zn	0.004	0.004 - 2

Each year the annual VWM for these metals are calculated using the following equation:

$$VWM = \sum_{i=1}^{n} X_i Y_i \; / \; \sum_{i=1}^{n} X_i$$

where X_i represents the sample volume in mL and Y_i is the concentration of the metal in mg L^{-1} collected at that respective site.

Precipitation is variable from year to year and from site to site, and the Great Lakes influence this precipitation variability as described by Changnon and Jones (1972) and Eichenlaub (1979). The annual precipitation amounts, calculated using a method developed by Barnes (1964) and modified by Achtemeier (1987), are furnished by the Illinois State Water Survey. Examination of this 8-year annual precipitation amount (1982-1989) compared to the 30-year mean (1951-1980) mean precipitation at the GLAD sites around the Great Lakes shows the 1982-1989 precipitation amounts to be greater than the 30-year average at 30 of the 35 sites.

After the annual VWM and the annual precipitation data are available, the annual loadings, expressed in kg km^{-2}, for all metals at all sites are then calculated. The sites have been grouped into either rural or urban sites according to the guidelines explained in the Introduction. A comparison of the VWM and annual loadings for the urban and rural sites has been completed. In addition the 8-year average monthly VWM for the sites was compiled to examine the monthly variation in metals data.

Table 2.--Atomic adsorption (AA) detection limits for metals in precipitation.T

Metal	Detection Limits (mg L^{-1})	Range (mg L^{-1})
As	0.00007	0.000007 - 0.0025
Cd	0.00013	0.00013 - 0.001
Cr	0.00007	0.00007 - 0.003
K	0.015	0.015 - 1.0
Na	0.010	0.010 - 1.0
Ni	0.00025	0.00025 - 0.003
Pb	0.0007	0.0007 - 0.010

RESULTS

The combined monthly 1982-1989 VWM data were examined for ten (10) metals (Pb, Fe, Ca, Zn, Cu, Cd, K, Mg, Na, and Ni). Except for Ca, Zn, and K the rural VWMs were less than those from the urban sites. Cd did not exhibit any pattern, and the urban maximum found in November is questionable.

The loadings trends of metals were variable. Sodium and Ca showed an increase in annual trends while Cd increased most notably at rural sites except for Lake Michigan. Potassium, Cu, Fe, Ni, and Zn loadings decreased from 1982 to 1989 while Mg loadings showed a general decrease during this same time period.

Lead is the metal which has shown the most noticeable reductions in loadings to the Great Lakes during this 8-year time period. The reason for the reduction in lead loadings is the mandatory use of unleaded fuel by automobiles in the United States as was pointed out by Eisenreich et al. (1986). Figure 1 is a plot of the annual lead loadings at three sites: Put-In-Bay (a downwind urban site) in western Lake Erie and Beaver Island (a rural site) and Evanston (an urban site) both on Lake Michigan. Data for lead is available from 1983-1989. This lead analysis was done by atomic adsorption (AA) spectrophotometry whereas in 1982 the precipitation samples were analyzed by inductively coupled argon plasma (ICP) spectrophotometry. The ICP had a much higher limit of detection, and therefore the data values were usually below minimum instrument detection limits.

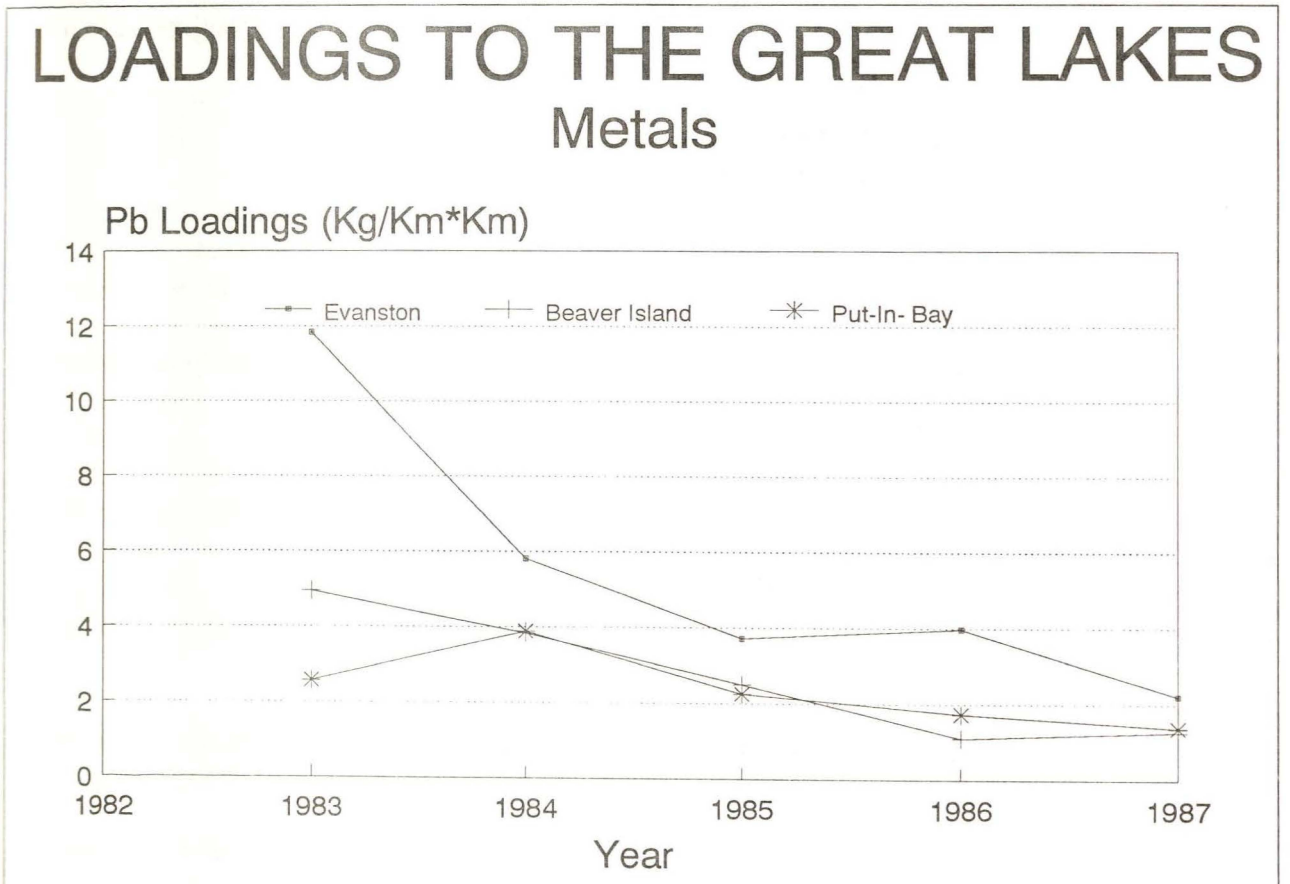

Figure 1. Pb loadings at selected sites

Figure 1.--Pb loadings at selected sites

CONCLUSIONS

Both the rural and urban 8-year VWMs for Pb, Fe, Zn, Cu, and Na show a maximum in the winter months and a minimum in the summer months. Potassium, Mg, and Ca, however, show maximums in the spring and summer while Ni and Cd show no significant pattern from month to month.

ACKNOWLEDGEMENTS

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TRACE ELEMENTS IN PRECIPITATION AT THE MIDDLE ATLANTIC COAST: A SUCCESSFUL RECORD SINCE 1982

T. M. Church and J. R. Scudlark[1]

ABSTRACT.--The trace elements Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se and Zn have been successfully measured in atmospheric precipitation events at Lewes, Delaware on the mid-Atlantic coast since 1982 as part of the NOAA-WATOX program. This constitutes probably the longest and most comprehensive trace element precipitation record in the United States. The concentrations exhibit large event and seasonal variation according to remote sources and local meteorology. This necessitates long and continual records for accurate analysis of concentration and flux trends. The patterns of enrichment relative to crustal elements are concordant with local and remote aerosol records suggesting common emission sources and scavenging after long range transport. The long-term average fluxes are consistent over the region and document the continual decline of some emission enriched elements such as lead over the past decade. The atmospheric fluxes of most trace elements, while a minor direct input term for estuaries, can dominate on the basis of the entire watershed. The atmospheric fluxes of many emission trace elements dominate the exported estuarine fluxes to coastal waters of the middle Atlantic region.

INTRODUCTION

Many atmospheric trace elements are co-emitted with sulfur and nitrogen during high temperature combustion. This results in the potential for the significant atmospheric mobilization and deposition of other elements in acid precipitation which may have equally important ecological implications.

Trace elements include both natural and anthropogenically derived metals such as Al, Cr, Fe, Mn and Ni which can have both mineral and metallurgical sources; As, Cd, Cu, Pb, Se, and Zn which can have primarily high temperature emission sources over industrialized continents from fossil fuel burning and industrial manufacturing.

Trace elements emitted and transported as micron-size aerosols largely fall out in the boundary layer near continental sources. However, many emission derived trace metals occur as submicron size aerosols which are scavenged from the troposphere primarily by precipitation. Thus trace metals in precipitation can be and are pervasive constituents of acid precipitation. Their transport

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and direct atmospheric deposition can constitute effective fluxes into continental or coastal watersheds with important ecological implications.

RATIONALE AND HISTORY OF COLLECTION

We initiated trace element collection at Lewes, Delaware in 1982 in an effort to expand our DOE-MAP3S major ion collections to other elements. Figure 1 is a map of the site, which is located within the semi-remote confines of Cape Henlopen State Park, in a sandy clearing among scrub pines a couple miles west of the Atlantic ocean beach.

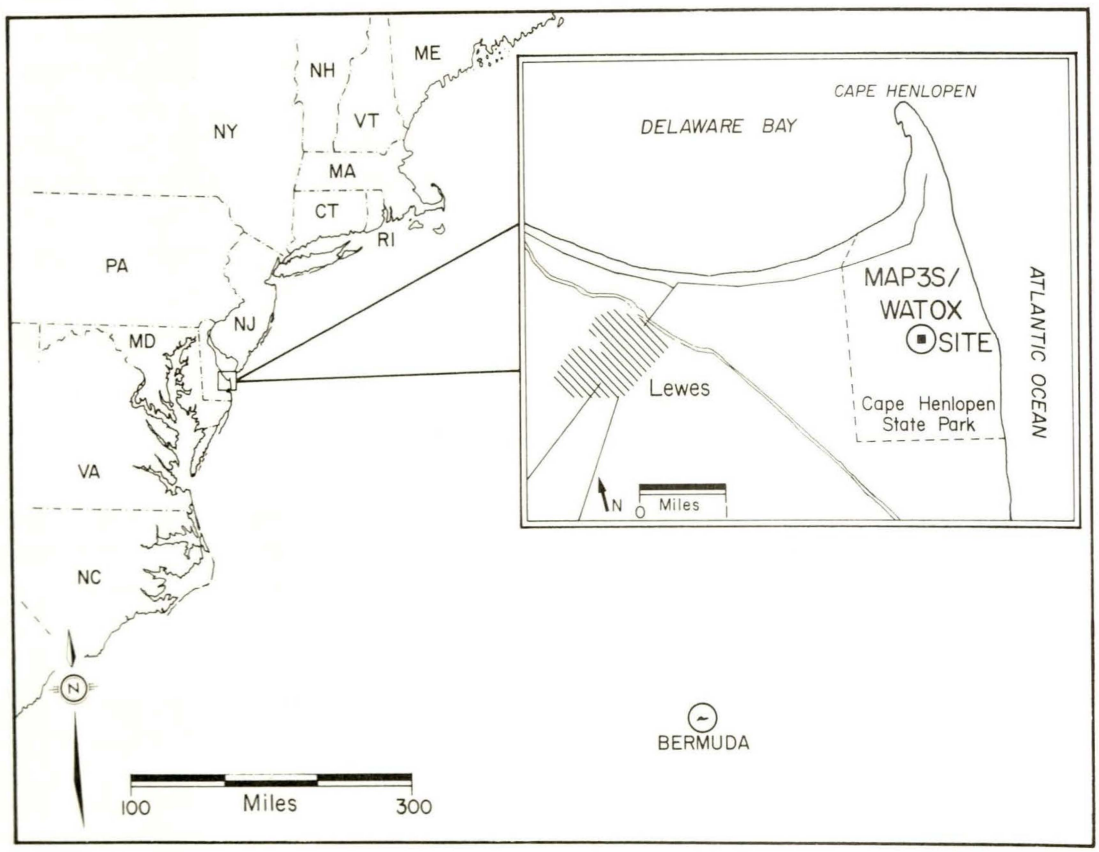

Figure 1.--Location of the atmospheric research station at Lewes, Delaware for the sampling of major and trace elements in precipitation.

Under the NOAA-WATOX program our general objectives were to document the source, transport, deposition and fate of North American atmospheric pollutants exported to the North Atlantic Ocean (Galloway et al. 1986). The collections at Lewes represented the coastal boundary end member for this effort, and the earlier results are published elsewhere (Church et al. 1982, Church et al. 1984). During this period (Table 1), several other researchers and programs took advantage of our site and research at Lewes to carry on related atmospheric studies at a semi-remote coastal location.

Table 1.--Chronology of atmospheric research at the Lewes, Delaware site located at Cape Henlopen state park on the mid-Atlantic coast-sponsoring agencies.

Dates	Research Activities
8/77-3/78	Initial site evaluations
3/78	Precipitation collections for major ions commenced (MAPBS)-DOE
4/81	OSCAR study (primary and 4 satellite stations) - DOE
5/82	Precipitation collections for trace metals started - (WATOX) - NOAA
8/82 & 2/83	WATOX Intensives--pollutant aerosols and gases (with General Motors, U. Miami, RSMAS, NRL)
8/23	Metalloid (As and Se) speciation study with G. Cutter (ODU)
2-4/85	WATOX Winter Intensive (AES Canada, NOAA-ARL, U.Wash., U. Virginia, NRL, York Univ.
2-3/86	GALE Extended Precipitation Network Site-
6/86	Tidal Wetlands Study NASA
9/87	AEROCE (NSF) Study commences - NSF
4 & 10/89	AEROCE related cruises (R/V Cape Hartteras)
7/89	Precipitation aerosol scavenging intensive, G. Gordon, (U. MD) - Md. Power Plant Res. Prog.
6/90	Chesapeake Atmospheric Toxics Deposition Network initiated - EPA

The rationale and procedures of our collection protocols and analytical techniques were published previously (Tramontano et al. 1987), and are updated in the companion paper by Scudlark et al. (1992, this volume). The analytical method is derived largely from our associated work in local salt marsh, estuarine and coastal waters. Here our objectives have been to evaluate the source and transport of trace metals from the land to the sea, and specifically to include atmospheric processes.

OBJECTIVES

The specific research objectives of our Delaware laboratory by collecting precipitation for trace elements in the Middle Atlantic region are to:

(1) determine the continental or marine source of trace elements and associated acid species using local meteorological and air mass trajectory information

(2) assess the short and long-term variability relative to atmospheric sources and fluxes

(3) measure the wet and estimate the dry atmospheric fluxes of trace elements to local estuarine and coastal waters relative to the mass balance from other fluvial sources

(4) provide a precipitation record useful for other state and federal projects interested in the possible environmental, health or ecological implication for the atmospheric deposition of trace elements in precipitation.

Application of the early part of the trace element precipitation record to these objectives has been published elsewhere (Church et al. 1986, Church 1986, Church 1988, Church et al. 1988) and will be updated in this paper. Generally, the early results showed that although trace element concentrations in coastal precipitation were greater than local rivers, estuaries, and bays, their direct atmospheric influx was minor in amount yet significant in proportion. However, considering the larger catchment areas of drainage basins and the indirect inputs to coastal waters, atmospheric trace element deposition primarily from precipitation was major and significant.

RESULTS AND DISCUSSION

CONCENTRATIONS

The average volume weighted concentrations and corresponding wet flux of trace elements from precipitation at the Lewes site for the eight year record (1982-1989) are shown in Table 2. While crustal elements (Al, Fe) dominate, non-crustal elements (e.g. Zn) are nearly as abundant, and generally most all trace elements are significantly more concentrated in precipitation than other continental surface waters. A limited (one year) data record at sites on the upper eastern and western shores of Chesapeake Bay (Scudlark and Church, unpublished data) show very similar concentrations suggesting long range sources and transport of most precipitation trace elements to the mid-Atlantic region.

The range of the monthly concentration of most elements (e.g., Al; Fig. 2) over the past eight years at Lewes is quite large (1-2 orders of magnitude) and show some cyclic trends. Aluminum generally peaks in spring coincident with regional agricultural tilling.

Table 2.--The long-term volume weighted average concentration and flux of trace elements in precipitation at Lewes, Delaware from 1982-1989.

	Concentrations		Wet Flux (110 cm H_2O yr^{-1})	
Element	ppb (µg L^{-1})	n Molar	ng cm^{-2} yr^{-1}	µmoles m^{-2} yr^{-1}
Al	26.2	970	2880	1070
Cd	0.098	0.87	10.8	9.61
Co	0.510	9.81	56.1	10.8
Cu	0.760	12.3	83.6	13.2
Fe	15.3	273	1680	301
Mn	1.24	22.6	137	25
Ni	1.12	19.0	123	21
Pb	1.9	9.17	209	10.1
Zn	5.16	78.9	568	86.9

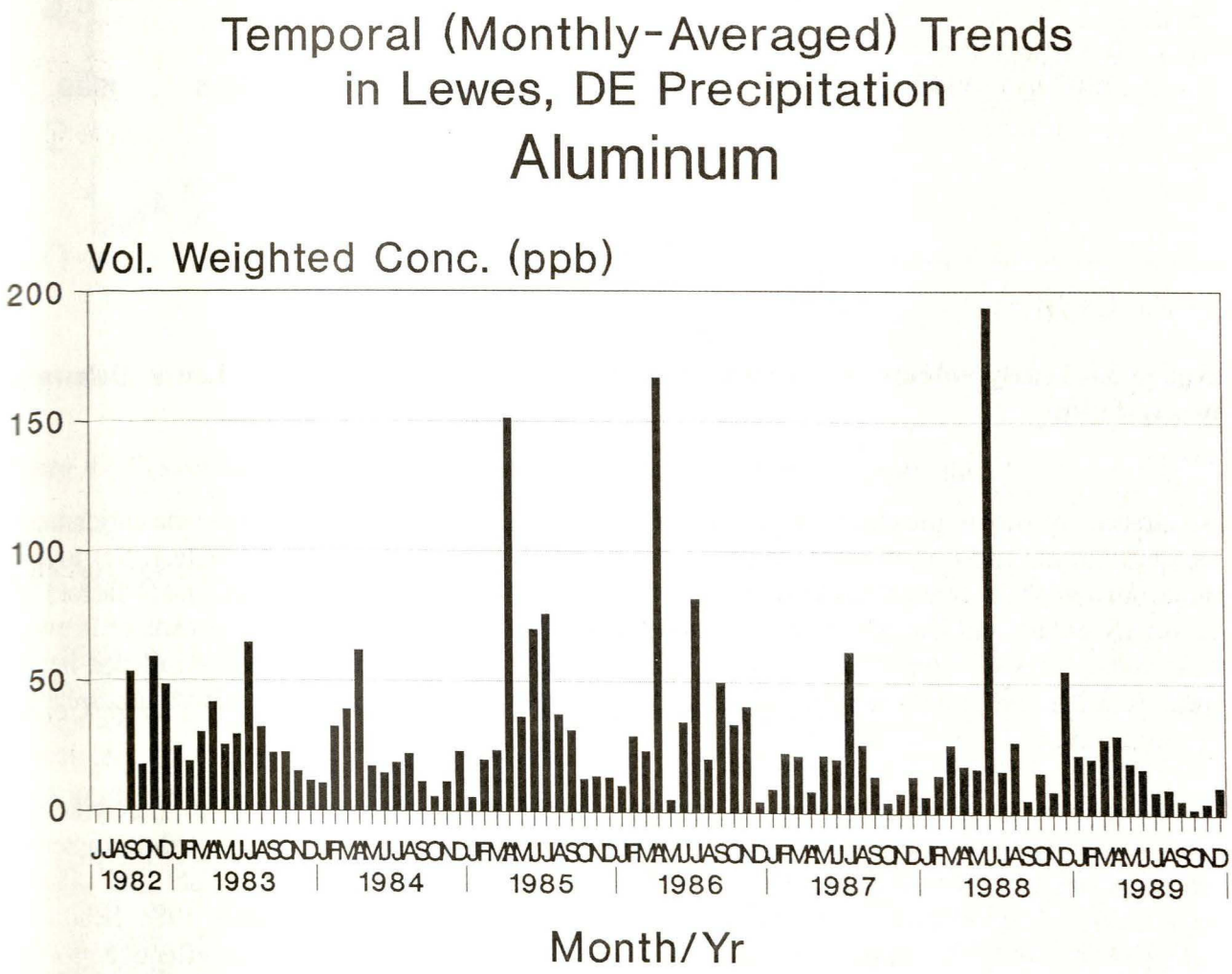

Figure 2.--Monthly volume weighted mean concentration of Al in Lewes, Delaware precipitation.

The yearly volume weighted mean concentrations of Cu is level, while Pb shows a gradual long-term decline coincident with the phasing out of leaded gasoline in the U.S. (Figure 3).

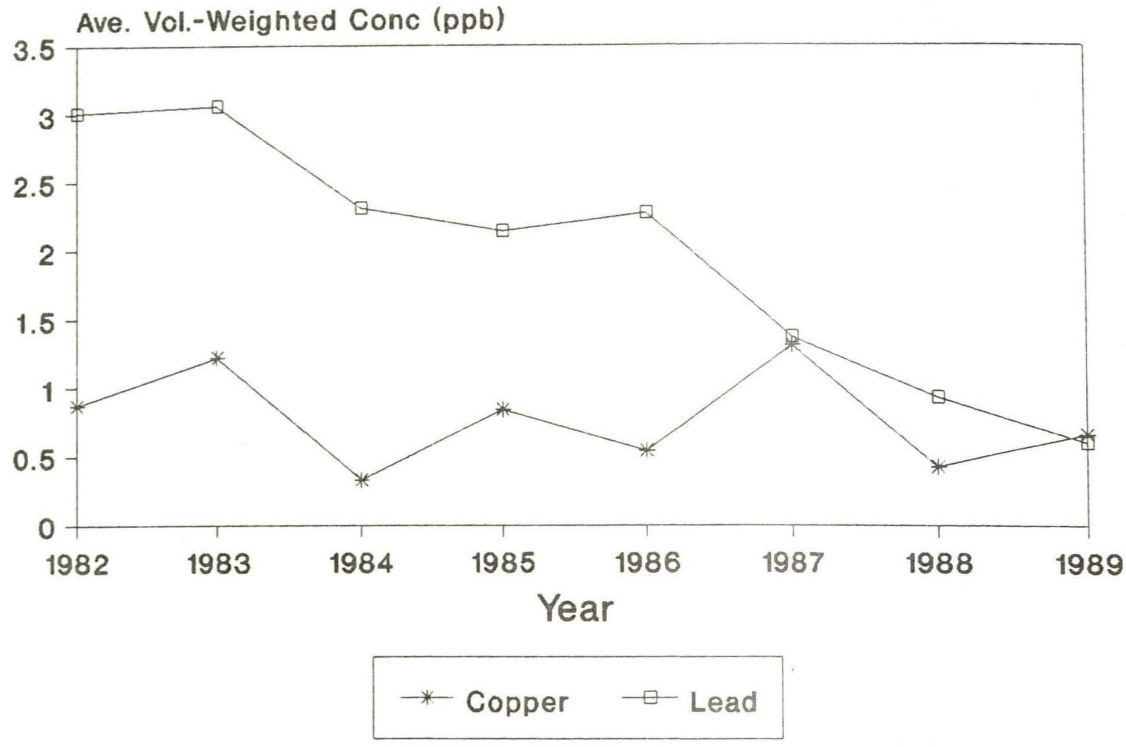

Figure 3.--Yearly volume weighted mean concentration of Cu and Pb in Lewes, Delaware precipitation.

An alternative way to present precipitation and aerosol concentration data is to use the enrichment factor (EF), the ratio of an element in the precipitation over a crustal reference (e.g. Se) to the same ratio in the reference material (e.g. crustal rock). The precipitation enrichment factors at Lewes (Scudlark and Church 1988) are nearly identical to those found in local aerosol, or in even more remote marine areas. This globally pervasive sequence in aerosols and precipitation bears witness to the common volatility, transport and deposition via precipitation of most atmospheric trace elements.

The good correlation of some trace elements to acid species in Lewes, Delaware precipitation points to a common source of some metals and acid species. By example, Figure 4 shows arsenic versus protons. Similar correlation of the metalloids Se and As with sulfate and nitrate respectively identifies coal combustion as a primary source (Cutter and Church 1986, Scudlark and Church 1988). In addition the redox species of these elements can act as effective probes of the redox conditions for those reactions coincident with cloud scavenging. For example the

oxidation of S (IV) to S (VI) is analogous to the oxidation of Se(IV) to Se(VI). Likewise the oxidation potential for NO_x conversion is coincident with that for As(III) oxidation.

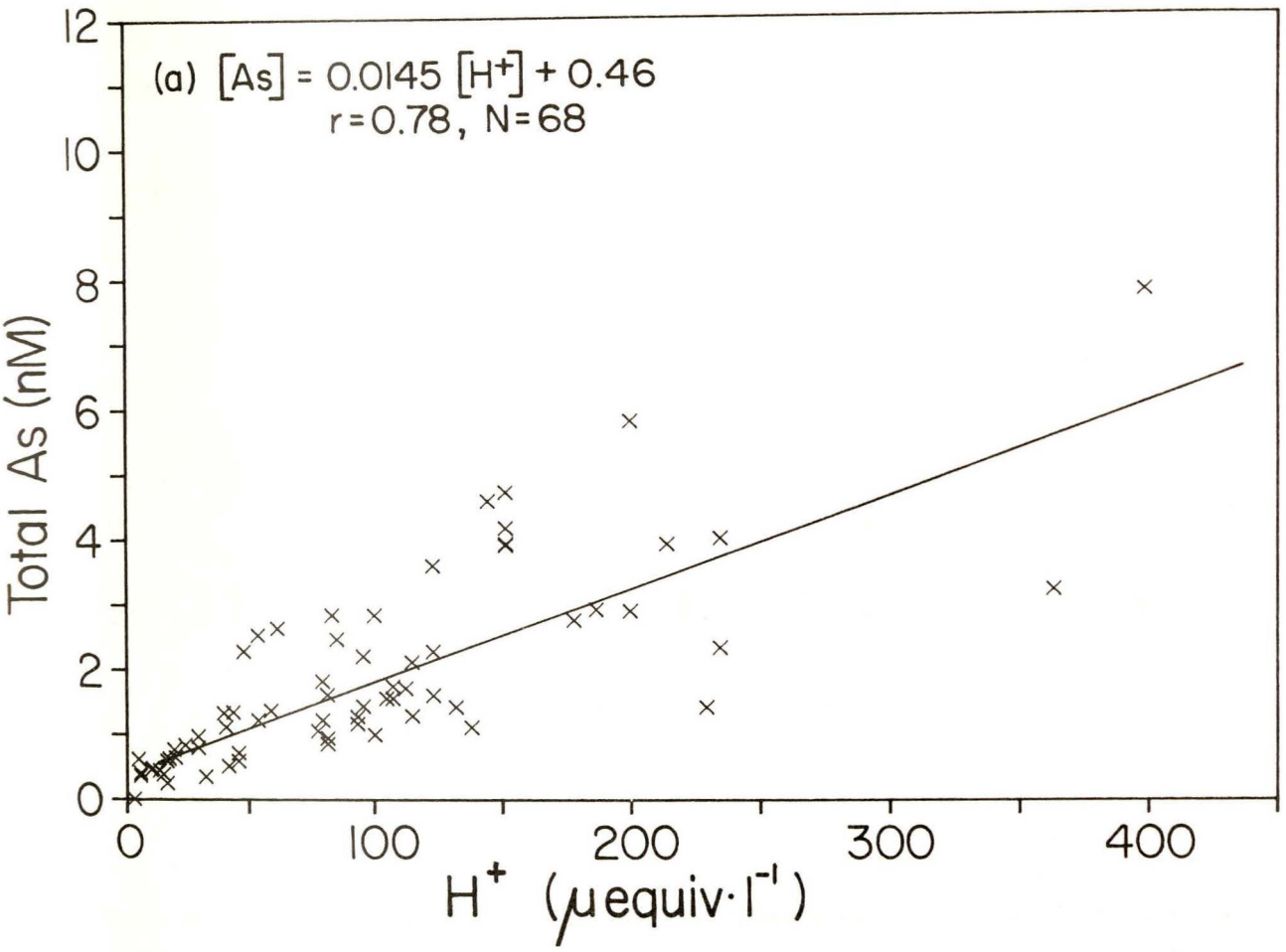

Figure 4.--Correlation of As and protons in Lewes, Delaware precipitation.

FLUX SOURCES

It is instructive to stratify wet deposition trace element data at Lewes, Delaware according to sectors of air mass trajectory during the events. The NOAA-ARL isobaric trajectory analysis corresponds to marine, southeast, midwest, and northeast sectors. Many coastal storms cannot be sectored and remain undefined. In Figure 5, the concentration and flux sectors for Se are given as an example.

Generally the sector flux patterns are similar for most trace elements, whereby the marine sector contributes the lowest flux while the southwest or midwest sectors contribute the most. Anthropogenic combustion and industrial sources are concentrated to the west and southwest, primarily from coal fired electrical power production and metal refinement.

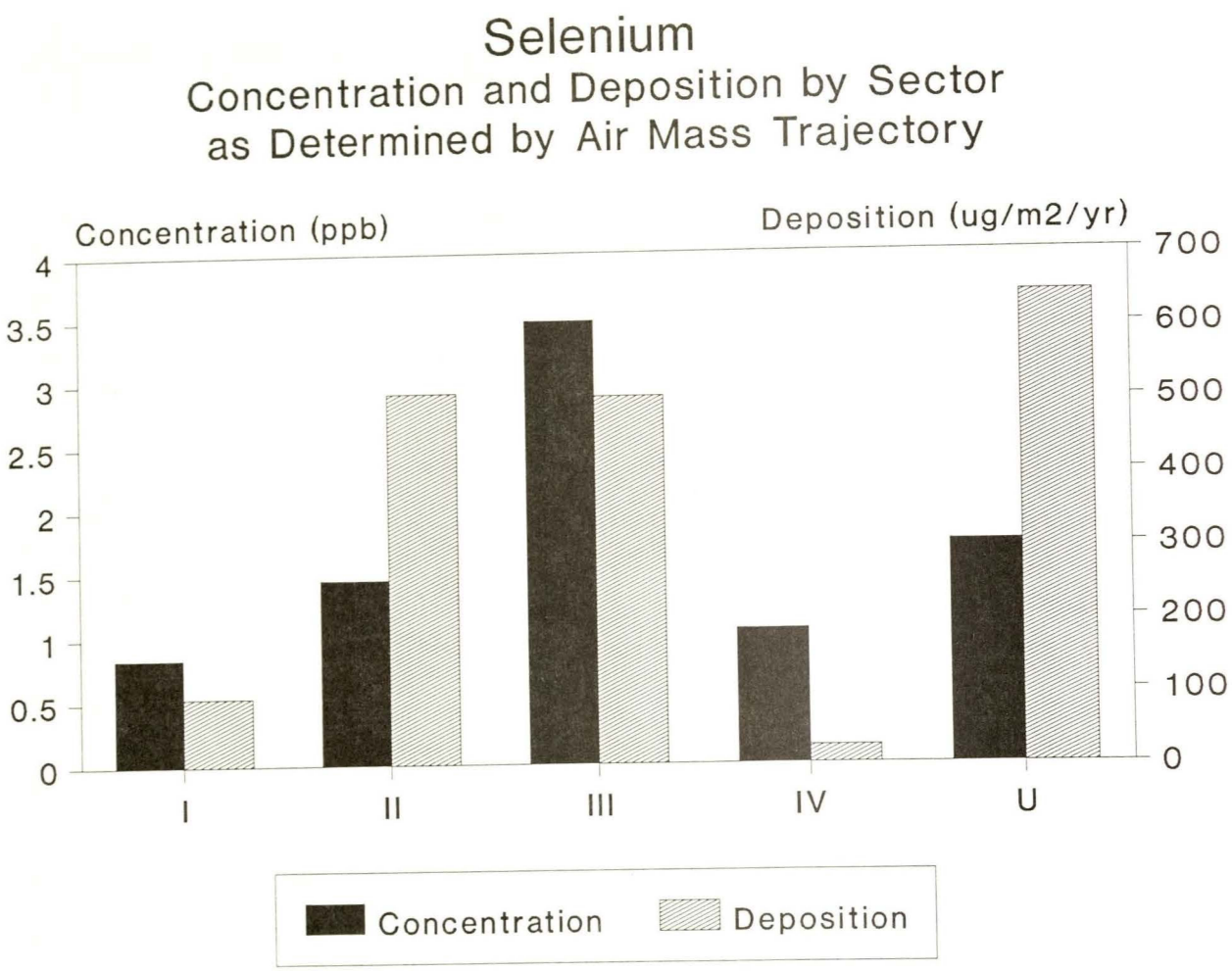

Figure 5.--Concentration and flux of Se in Lewes, Delaware precipitation sectored according to air mass origin I (marine), II (southeast), III (midwest), and IV (northeast), and U (undefined).

FLUX MODELING

The atmospheric flux of trace elements by precipitation can be put in perspective with other fluxes to coastal water bodies. First, however, the wet fluxes measured in Lewes, Delaware precipitation (Table 2) must be added to dry fluxes which have not been measured. Dry fluxes can be estimated from aerosol concentration at Lewes, Delaware measured during WATOX intensive experiments (summarized in Wolff et al. 1987). These aerosol concentrations represent the average of nearly 70 samples collected over two six week periods during August 1982 and February 1983. The aerosol concentrations can be partitioned into crustal components using Al as a normalizer, with the excess constituting the non-crustal component. The crustal component is assigned a deposition velocity typical of soil dusts (0.3 cm/sec) and the non-crustal component one typical of accumulation mode aerosols (0.1 cm/sec). The calculated total dry deposition of

trace elements is added to the measured wet deposition to give an estimate of the total atmospheric deposition (Table 3).

Table 3.--Dry and total atmospheric flux (ng $cm^{-2}yr^{-1}$) at Lewes, Delaware.

Element	Aerosol ($ng\ m^{-3}$)	Dry Flux			Wet Flux[1]	Total Flux
		Crustal	Non-crustal	Total		
Al	432	4040	--	4040	2880	6920
Cd	<1	--	<1	<1	10.8	11
Cr	12	7.7	55	63	56.1	119
Cu	4.5	1.9	13	15	83.6	98.6
Fe	149	1390	0	1390	1680	3070
Mn	4.7	43	0.4	43	137	180
Ni	5.4	3.7	5.6	9.3	123	132
Pb	63	1	197	198	209	407
Zn	32	4.7	83	88	568	656

[1] From Table--2.

The dry deposition component is only comparable to the wet component for the crustal elements (Al, Cr and Fe) which is consistent with their super-micron soil mode. However, the wet flux clearly dominates the total flux for all non-crustal dominated elements (Cd, Cu, Ni and Zn) which is consistent with their sub-micron accumulation mode as emission derived elements. We know the dry component for Pb is too high from inaccurate aerosol concentrations.

The wet flux of trace elements to the Delaware watershed (DEW) can be estimated using the Lewes, Delaware precipitation data and comparing it to that entering the Delaware Bay estuary from the river at Trenton (Church et al. 1988). The result shows that precipitation can contribute far more trace elements (except Mn) to the watershed than are needed to account for that entering its estuarine portions. The excess is evidently taken up in the watershed soils and ecosystems by aquatic reactions during run off.

The direct wet deposition flux of trace metals from precipitation falling into open waters of the Delaware Bay estuary (DEB) itself is minor to that entering from fluvial and tidal sources (Church 1986). This may be unrealistic when one considers that the fresh and tidal sources themselves may be directly derived from atmospheric deposition to their watersheds, or indirectly from chemical reactions of digenesis within their soils.

Table 4 summarizes by percentage the mass balance contributions of trace elements from wet and total atmospheric deposition at Lewes, Delaware.

The direct total atmospheric deposition to coastal waters of the Middle Atlantic Bight (MAB) can be compared to that estimated from the net tidal flux of the large estuarine river systems Chesapeake, Delaware and Hudson (Church 1988). These earlier estimates have been updated in Table 4 from the more recent seven year record presented in Tables 2 and 3. The percentage atmospheric input to the Middle Atlantic bight, while minor for some elements such as Cu and Mn, can be dominate for other elements such as Pb and Zn. Atmospheric delivery of trace elements to coastal waters is as important as delivery of major nutrients such as N.

Table 4.--The corresponding atmospheric percentages of trace metal deposition at Lewes, Delaware.

	----------Fluxes (%)----------		---------Atmospheric component (%)----------		
Element	Wet[1]	Dry[1]	DEW[2]	DEB[3]	MAB[4]
Al	42	58	--	--	--
Cr	98	2	--	--	--
Cd	47	53	--	--	--
Cu	85	15	41	4	18
Fe	55	45	64	2	--
Mn	70	24	-58	0.1	4
Ni	93	7	43	2	30
Pb	51	49	--	--	96
Zn	87	13	32	4	64

[1] Relative percentage of the total flux.
[2]Percentage wet flux surplus of the Deleware watershed (DEW) to the fluvial component entering Deleware Bay (DEB).
[3]Direct atmospheric input to the total including all fluvial and tidal sources to Delaware Bay (DEB)
[4]Direct atmopsheric input to the total including net estuarine flux to coastal waters of the Middle Atlantic Bight (MAB). See text for details.

CONCLUSIONS

As for acid components, the concentration of trace elements in continental precipitation can be substantial. The range of concentrations can be very large depending on remote sources and local meteorology. The enrichments relative to crustal rocks and the sectoring of air mass sources suggest long range transport and deposition from emission sources to the south and midwest. The magnitude of the concentrations largely exceeds that of other surface waters suggesting that their atmospheric contribution from wet flux may be important. Indeed, mass balance calculations show that atmospheric deposition indirectly to the watersheds of Middle Atlantic estuaries or directly to the waters of the shelf is significant. This may have important implication to the ecosystems of these water bodies.

Future monitoring of trace elements in precipitation must be taken with considerable caution. The protocols for collection and the challenges of analysis will be demanding in dedication and resources. The places of collection must be well chosen and maintained; and, the collection maintained for a number of years to accurately average the variability of event fluxes. Nevertheless, the potential importance of the atmospheric wet deposition of trace elements will demand such monitoring.

ACKNOWLEDGEMENTS

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A METHOD FOR THE AUTOMATED COLLECTION, PROPER HANDLING AND ACCURATE ANALYSIS OF TRACE METALS IN PRECIPITATION

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ABSTRACT.--A method is described for the accurate determination of trace metals in precipitation, which has been successfully utilized for ten years at diverse rural and remote locations. The accurate determination of trace metals in precipitation at the nanomolar level (generally 3 or more orders of magnitude less than major ion constituents), requires the use of specific materials and exacting cleaning, handling, preservation and collection procedures. The total atmospheric wet deposition of trace metals is apportioned between dissolved and particulate phases, which varies spatially and temporally for each metal. The application of proper collection and analysis techniques insures quantification of the total (dissolved plus particulate) concentration.

INTRODUCTION

Within the past decade, atmospheric trace elements have come under increased scrutiny from a number of perspectives. The importance of the atmospheric transport and deposition of trace metals to aquatic and terrestrial systems has been well documented. Atmospheric trace metals have also been identified as important redox catalysts for aqueous phase S(IV) oxidation (Graedel and Weschler 1981, Conklin and Hoffmann 1988). Additionally, recent approaches have utilized atmospheric trace elements for emission source identification, using a variety of source-receptor modeling approaches (as reviewed by Gordon 1988).

In 1980, our laboratory began to address the routine monitoring of trace metals in precipitation as part of the MAP3S (DOE) and WATOX (NOAA) programs. For this we required a simple, automated, accurate procedure applicable to both rural continental and semi-remote island locations. Reviews of the historical data on the concentration of trace metals in continental precipitation (Galloway et al. 1982a, Barrie et al. 1987) cast considerable doubt on the reliability of reported values and the efficacy of the techniques utilized. In many of these studies, it was apparent that the authors failed to observe proper sampling and handling precautions (Batley and Gardner 1977, Ross 1986), resulting in either gross contamination, or conversely, irreversible losses of certain metals to container walls (Chan et al. 1983).

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On the other hand, we did not know if the meticulous precautions utilized in studies at remote locations (e.g. Arimoto et al. 1987) were necessary or practical for application in a long-term, routine monitoring mode. Thus, we proceeded to develop and test a technique for the automated collection, handling and analysis of trace metals in precipitation.

The procedures reported in this paper represent the ongoing evolution of our methodology as previously published (Tramontano et al. 1987). These methods have been successfully employed under a variety of conditions, including a continual (since 1982) record of trace metals in precipitation at the mid-Atlantic coast of the U.S. (Lewes, DE), reported by Church et al. in this volume and an ongoing study of the wet depositional flux of potentially toxic trace metals to Chesapeake Bay. The same technique has also been used in more remote locations such as Bermuda (Church et al. 1984) and Ireland.

PROCEDURES

The principal challenge in determining trace metals in precipitation is to minimize contamination of the sample during sampling, handling and analysis. Compared with acid rain protocols (e.g. Galloway 1978), this is considerably more difficult since trace metals are typically present at concentrations lower by 3 or more orders of magnitude than major ions, generally in the nmole/L range for most elements in continental precipitation. Thus, fastidious collection and handling procedures must be strictly adhered to; even contamination by airborne dust must be minimized. We emphasize the following two specific precautions to insure trace metal-clean techniques:

(1) All operations involving sample manipulation (collection, acidification, partitioning and analysis) must be performed wearing clean, powder-free polyethylene gloves. As a general rule, a new pair of gloves is donned when the surface to be touched is cleaner than the previously-handled surface.

(2) Sample manipulation, plasticware cleaning, and analyses should be performed in a clean area; we strongly recommend use of a Class 100 clean bench. Regardless, precautions should be taken to minimize exposure of the sample to airborne contamination.

PLASTICWARE

Materials only made of polyethylene, Teflon^{R} (Reg. TM E.I. duPont de Nemours & Co.) and polypropylene should be used for sampling, storage and laboratory manipulation. Of these, Teflon^{R} is the preferred material for trace metals studies (Batley and Gardner 1977), but is prohibitively expensive for large-scale use. "Virgin" LDPE (low density polyethylene polymerized directly from ethylene gas) is a practical alternative for transition metals, as the comparatively permeable plastic matrix allows for efficient metal leaching during cleaning and sample desorption steps (Batley and Gardner 1977, Subramanian et al. 1978). However, for the metalloids (Se, As, Sb etc.), which in contrast to most metal cations are in theory present in

precipitation as oxy-anions, irreversible losses to the container walls have been reported for LDPE (G. Cutter, pers. communication); for these elements, less pervious HDPE is the preferred plastic, (although, this artifact is probably insignificant at concentrations typical of most U.S. continental precipitation).

The standard white polyethylene bucket used in acid rain studies is absolutely not suited for trace metals studies. To demonstrate the inaccuracy resulting from samples obtained in standard white acid rain buckets, we conducted a side-by-side comparison of samples from 26 events, collected according to standard major ions protocols and our trace metals methods as presented here. (Samples from the major ions collector could obviously not be acidified until partitioned into storage bottles). A comparison of the mean concentrations calculated from samples collected by each method (Table 1) shows that Cd and Zn were severely contaminated (>100%) and Cu moderately contaminated in the major ion sampler. In contrast, Pb exhibited significant adsorptive loss in the major ions bucket. Thus, it is clear that except for Fe and Mn (which are of little interest from a toxicological perspective), samples collected according to standard major ions procedures cannot be utilized for trace metal determinations.

Table 1.--Comparison of mean trace metal concentrations from simultaneous collections utilizing major ions/acid rain protocols with trace metal methods as presented in this paper.

Collector	Cd	Cu	Fe	Mn	Pb	Zn
	mean concentration ($\mu g\ L^{-1}$)					
Major Ions	0.320	1.20	10.24	1.79	1.46	15.66
Trace Metals	0.116	0.78	11.59	1.63	3.14	4.57

For sample collection, we currently utilize a clear, 17 liter HDPE bucket and snap-fitting lid (Rubbermaid #2618), cleaned according to the procedures outlined in Table 2 (which are subsequently discussed). This bucket has a slightly larger effective capture area compared with the white major ions bucket (730 vs 682 cm^2), but is compatible with the ACM collector without modification.

In the past, we have also utilized an appropriately cleaned, heavy gauge (4 mil), 10 x 8 x 24 in. round-bottomed, LDPE bucket liner (Associated Bag Co., Milwaukee, WI) for sample collection (Good and Schroeder 1984). For installation, the top of the bag is folded over the lip of a major ions bucket, and the air under the bag is evacuated by applying a vacuum via a small hole near the bottom corner of the bucket. Although bucket liners are inexpensive, expendable and easy to ship to remote collection sites, we found them to be difficult to properly clean and install according to trace metal protocols, as evidenced by blank levels which were consistently higher

than buckets. In addition, we found that bag liners were not always reliable in the field, due to leakage (resulting from manufacture, cleaning or puncture by post-depositional ice formation) and the tendency of the bag to blow out of the bucket in high winds.

REAGENT ACIDS

To prevent (or reverse) the adsorptive loss of trace metals from the precipitation sample onto the plastic surfaces of collector bucket and storage containers, standard laboratory practice is to acidity samples to a pH <2 (Struempler 1973; Subramanian et al. 1978). HNO_3 is the most commonly used acid for this purpose, but its use might be discouraged where cross-contamination with parallel acid rain collections poses a potential problem. To avoid any possible contamination, we have substituted HCl. Regardless of the acid employed, it is imperative to utilize ultra-high purity acid (i.e. low trace metal content). This can either be prepared in-house by doubly re-distilling reagent grade acid in a Teflon^R or quartz sub-boiling still, or purchasing a commercially-available equivalent. With our doubly-distilled acid (which we refer to as Qz-HCl), acidification to 0.4% (v/v) results in a 0.05 N solution, which is sufficient to lower the pH of poorly-buffered precipitation below 2. It should be noted however, that with few exceptions (e.g. Se), acidification precludes metal speciation studies.

CLEANING

To minimize sample contamination from metals introduced via manufacture (impurities from catalysts, promoters or metal dies) or prior use, all plasticware must be rigorously cleaned. Such impurities can exist adsorbed onto the plastic surface or within the plastic matrix (Karin et al. 1975). Although many variations on trace metal cleaning procedures have been reported, all involve leaching with acid (HCl and/or HNO_3) of varied strengths and duration. The cleaning procedure we utilize is outlined in Table 2. Ultrapure rinse water (ASTM/CAP/NCCLS Type I, having a resistivity consistently in the 18 megohm/cm range) should be used throughout. In our laboratory we utilize Milli-Q^R (Reg. TM Millipore Corp.) reagent grade water, and subsequently refer such water as Q-H_20. To preserve the activated adsorption sites on the freshly-cleaned plastic surface, we store sample bottles with a small amount of 0.1% Qz-HCl (enough to cover the bottom).

Due to their relatively high cost (ca. $10), we reuse trace metal buckets by either recleaning them on site or alternatively, recycling them back to the centralized laboratory for re-cleaning. For on-site recleaning between precipitation events, a less rigorous procedure is required (Table 2, steps 1, 2, 9-12); however, we recommend periodically (semi-annually) returning the buckets to the central laboratory for a more thorough cleaning.

Table 2.--Cleaning procedure for plasticware utilized for the collection, storage and analysis of trace metals in precipitation.

1.	wash with soapy water
2.	rinse 3 times with Q-H_20
3.	rinse with reagent grade acetone
4.	shake off excess acetone and rinse 3 times with Q-H_20
5.	soak in 6N reagent/ACS grade HNO_3 for 3 days
6.	rinse 3 times with Q-H_20
7.	soak in 10% reagent/ACS grade HCl for 3 days
8.	rinse 3 times with Q-H_20
9.	soak in 0.4% Qz-HCl for 3 days
10.	rinse 3 times with Q-H_2O
11.	fill sample bottles with a small amount (enough to cover bottom) of 0.1% HP-HCl and cap tightly
12.	seal all plasticware in doubly-bagged, clean LDPE bags

PRECIPITATION COLLECTOR

For trace metals sampling, the collector siting criteria utilized for any precipitation chemistry study should be adhered to. To further minimize "splash-off" from the collector into the bucket during sampling, we orient the wet bucket to face upwind relative to the prevailing wind direction (west) during typical precipitation events at our site.

It is necessary to dedicate a separate collector for trace metals studies due to several significant collector modifications, and incompatibilities in collection buckets and handling protocols with major ions (acid rain). However, trace metals collections can otherwise be conducted in parallel with acid rain sampling. We have utilized the Aerochem Metrics (ACM) Model 301 (Aerochem Metrics, Inc. Bushnell, FL) wet-only collector. Since the ACM collector is widely used in acid rain studies, most site operators are familiar with its operation and repair, and it is convenient to keep an inventory of spare parts on hand which can be used with either collector. Additionally, use of identical major ions and trace metal samplers insures comparable collection (capture) efficiencies, which is an important consideration for subsequent data comparisons. In fact, it is advisable and relatively simple to connect both collectors to a single rain sensor.

For trace metals determination, the ACM collector must be factory-equipped with the following important modifications:

(1) Teflon^R-coated lid support arms, to minimize contamination from "splash-off" during rain events;

(2) polycarbonate lid, for the same purpose as above. A peaked polycarbonate snow roof is also available where necessitated by the amount of snowfall.

(3) "old" style (about 26 cm. high) bucket holder, which accommodates the required collection buckets without further modification; and

(4) removal of the dry side bucket, which prevents contamination of the lid seal and "carry-over" of dry deposited trace metals from the rim of the dry bucket to the clean wet bucket (we remove the entire bucket holder).

As an independent verification of collection efficiency and accuracy of the automated collector, we used a side-by-side manually deployed (MD) collector. The MD sampler was carefully covered and exposed to achieve a high (>99%) collection efficiency and to avoid the inadvertent capture of dry fallout during non-precipitating periods. This collector consists of a HDPE funnel (surface area 600 cm^2) screw fitted with a watertight, threaded Teflon^R (TFE) coupling to a 1-L Teflon^R (FEP) bottle. This sampler design has been used in the NOAA Global Precipitation Chemistry Project (Galloway et al. 1982b). Comparisons of concentrations from the two collection methods were made on 25 occasions at Lewes, DE and High Point, Bermuda. For all metals, the data were highly correlated (r^2>0.88) with slopes close to 1.0; the volume-weighted average concentrations from each collector (Table 3) were also in accord. Thus, we believe that precipitation collected with the modified ACM collector accurately reflects the wet depositional flux of trace metals.

Table 3.--Comparison of volume-weighed mean concentrations from a manually-deployed (MD) and automated (ACM-TM) collector, sampled in parallel.

COLLECTOR	Cd	Cu	Fe	Mn	Pb	Zn
Lewes, DE						
ACM-TM	0.172	1.18	16.4	1.40	3.17	5.39
MD-TM	0.133	0.81	18.2	1.62	2.80	4.69
High Point, Bermuda						
ACM-TM	0.041	0.223	6.21	1.10	0.48	1.30
MD-TM	0.043	0.261	7.56	1.08	0.50	1.62

COLLECTOR DEPLOYMENT, RECOVERY AND SAMPLE PROCESSING

While retrieving samples or deploying collection buckets, we recommend standing downwind from the bucket to minimize potential contamination from the site operator. Wearing clean gloves, the bucket (with lid attached) is removed from its bag, and placed in the holder on the collector. As the collector lid moves back to cover the bucket, the bucket lid is removed, returned to its bag and sealed with a twist-tie. This process is then reversed for sample retrieval, with a clean bucket deployed at the same time. We also recommend cleaning the underside of the collector lid (which contacts the bucket) with a clean, wetted Precision Wipe^{R} (Reg. TM Scott Paper Co.), or equivalent low-lint, low-trace metal lab wipe.

In the designated clean area in the laboratory, the sample weight is determined by subtracting the tare weight of the empty bucket and lid. Uncovering the bucket only slightly (1/2"), the appropriate amount of Qz-HCl is added with an adjustable auto-pipette and acid-cleaned disposable tip to make the final concentration 0.4% (v/v), i.e. 4 mL of acid per liter of sample. As previously discussed, this step insures the quantitative desorption of metals from the collection bucket walls back into solution. It is not advisable to pipette directly from the primary acid supply, but rather, to utilize a small sub-aliquot for day-to-day use. Where appropriate clean facilities and/or high purity acids are not available, it is possible to freeze precipitation samples directly in the collection bucket, for subsequent acidification and processing at the centralized laboratory.

After a 24-hr. desorption period, the sample is homogenized by swirling the bucket, and partitioned into pre-cleaned, triply-rinsed storage bottles. (The 0.1% Qz-HCl storage solution should be first discarded). It should be noted that when volume limited, three small rinses are more efficient than one large rinse of equal volume. The bottles should be tightly capped, and doubly sealed in plastic bags pending analysis. Depending on the inventory of elements to be analyzed, the minimum volume requirements for trace metals analysis is similar to major ions (ca. 50 mL for the suite of standard transition metals). For metalloids and/or other elements with larger analysis requirements, we save a maximum of 2 liters of sample. Samples should be refrigerated, or preferably frozen, until analysis.

ANALYSIS

The two most commonly-employed methods for trace element analysis of natural waters are graphite furnace atomic absorption spectrophotometry (GFAA) and inductively-coupled plasma emission spectroscopy (ICP). Except for a few elements (Al, Fe, Mn, Zn), only GFAA exhibits adequate detection limits for the direct determination of trace metals in precipitation at concentrations typical of rural U.S. regions. However, with sample preconcentration by evaporation (-20X), ICP offers a viable alternative to GFAA (Keller et al. 1988, Jickells et al. 1991). In fact, as is subsequently discussed, for elements derived predominantly from crustal sources (Fe, Al), ICP may yield more accurate results.

Some elements of interest from a toxicity perspective (e.g. As, Se, Hg) are present in precipitation at concentrations well below the detection limits of commercially available atomic absorption/hydride techniques. For example, the average As concentration in Lewes, DE precipitation (1.3 nmole L^{-1}) is significantly less than both atomic absorption (-7 nmole L^{-1}) and ICP (-20 nmole L^{-1}) hydride detection limits. Accurate quantification of these elements requires the application of state-of-the-art analytical techniques (e.g. Cutter et al. 1991) and larger minimum sample volume requirements.

Our laboratory has routinely utilized GFAA for the determination of Al, Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn in wet deposition. Although the relatively simple chemical matrix of precipitation greatly facilitates GFAA analyses, for some elements specialized techniques are required to compensate for chemical interferences. For example:

(1) the Pb signal is significantly suppressed by salts, thus requiring analysis using a L'vov platform (which eliminates matrix suppression by delaying atomization);

(2) since we utilize HCl for sample acidification, the char/ash step is limited to 170°, to prevent volatilization of $AlCl_3$ (b.p. 185°);

(3) increased analytical sensitivity for Al and Fe is achieved by the addition of cirtic acid as a matrix modifier.

QA/QC PROTOCOLS

A strict adherence to a rigorous quality assurance / quality control (QA/QC) program is essential to establish and maintain data accuracy. Elements of this program include the use of:

(1) externally certified reference solutions (e.g. EPA, NIST) which are included in every analytical session;

(2) inter-lab analytical comparisons;

(3) operational blanks on a regular (bi-monthly) basis and/or if there is a significant change in methods, reagents (e.g. a new batch of acid), land use around the site (e.g. excavation) or personnel (a new or substitute site operator).

OPERATIONAL BLANKS

In order to accurately quantify background trace metal levels and to identify and remedy sources of contamination, we strongly advocate the use of procedural blanks. We use three types of additive blanks to identify, quantify and remedy any source of contamination:

(1) A process blank, which consists of a 250 mL sample bottle containing Q-H_20 and Qz-HCL only. This is a measure of the trace element contribution derived from the acid spike, leaching from the storage bottle, and analytical procedures.

(2) A laboratory blank, which consists of a 250 mL Q-H_20 spike added to a clean sample bucket in the laboratory, acidified, and decanted into a sample bottle after a 24-hr. desorption period. The lab blank gauges the trace metal contribution from all sources embodied in the process blank, as well as metal leached from the collector bucket and airborne contamination during partitioning.

(3) A field blank, which is conducted identically to the lab blank, but using a bucket which was previously deployed in the collector during a non-precipitating period for a representative sampling interval (e.g., 2-5 days for event sampling or 7 days for weekly integrated sampling). The field blank includes trace metal input from all sources included in the lab blank, plus metal contribution from field operations such as the input of fugitive dust to the sample bucket during transport, deployment and recovery.

For most metals, the majority of the blank contribution is from materials and reagents, as represented by the laboratory blank. For Al, Fe, and to some degree Mn, which have predominant crustal sources, the field activities provide the major blank contribution. However, since the field blank is the most representative of sampling conditions, it is used to correct apparent precipitation concentrations. This correction is usually only required when the blank contribution exceeds 10% of the average metal content in corresponding precipitation (an approximate limit of analytical confidence).

A comparison of absolute blank levels and relative blank contributions to precipitation [(nmoles blank/nmoles in average precipitation sample) x 100%] at three sites using the sampling protocols under varying conditions is presented in Figure 1. For the Lewes site, sampling on a daily basis under optimal conditions and with an experienced operator, the field blank is only utilized qualitatively for diagnostic purposes. At Bermuda, also sampled daily, the blank levels are lower for most elements (probably due to cleaner environmental conditions), although the very low precipitation concentrations require that the field blanks be used quantitatively for some elements (Pb, Cd, and Zn) to accurately determine true rainwater concentrations. At the Chesapeake Wye site, precipitation is sampled in parallel (weekly integrated) with the NADP collector. However, without an available clean bench for sample processing or the same level of operator expertise as the Bermuda and Lewes sites, the blank levels are significant for a number of metals (Cd, Cu, and marginally Zn).

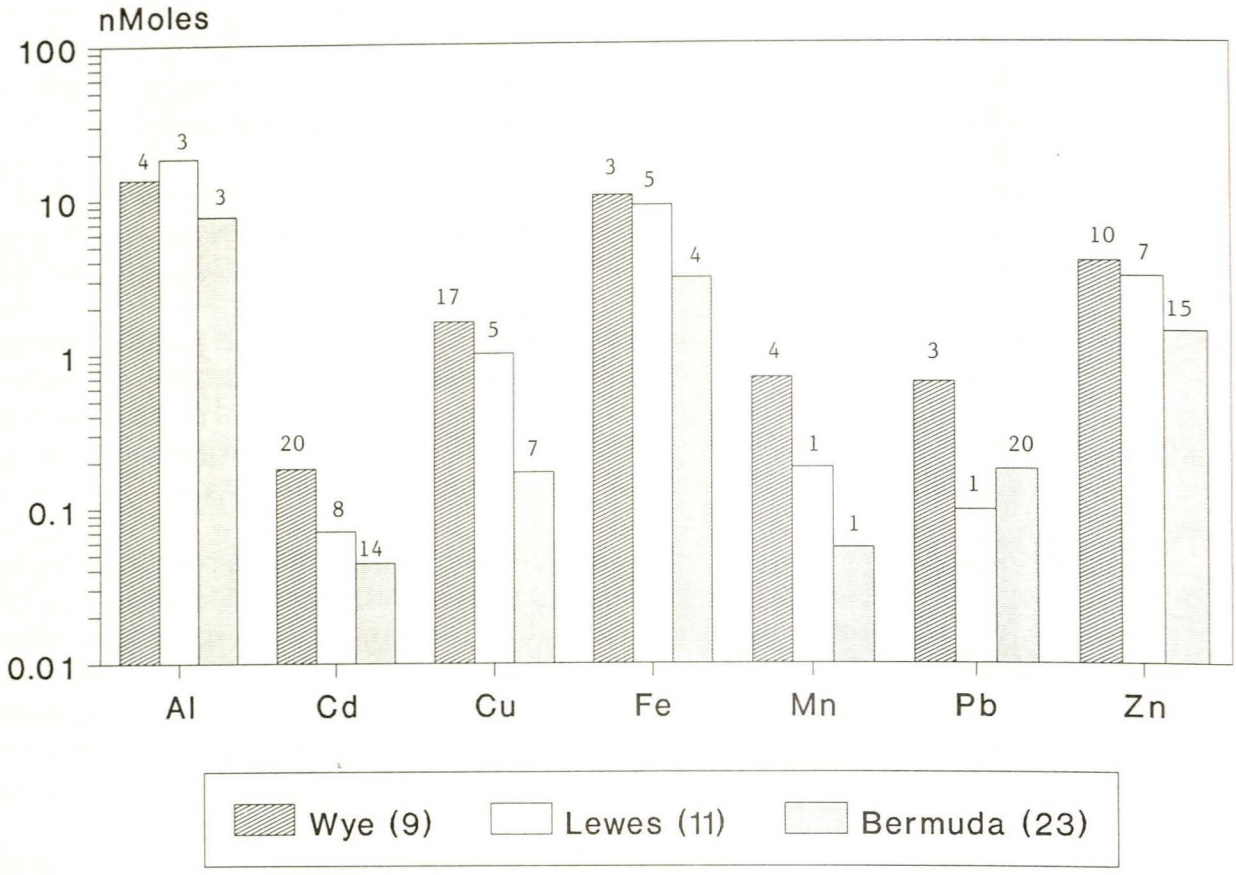

Figure 1.--A comparison of absolute field blank levels (nmoles) at three sites. Numbers above each bar refer to the average field blank contribution (%) to precipitation at each site.

This is probably representative of typical blank levels that could be expected under these conditions, and underscores the critical importance of determining accurate blanks under variable field and meteorological conditions at each site.

It is important to bear in mind that whether sampling or conducting blanks, the objective is both to minimize contamination as well as maintain it at a consistent level for accurate blank correction. This emphasizes the need to utilize uniform reagents, materials and sample handling procedures. Thus, to maintain constancy, blanks should be conducted with the same degree of caution as normal sampling.

TRACE METAL SOLUBILITY IN PRECIPITATION

Trace metals may be introduced into the atmosphere via resuspended soil and from high temperature emissions of both natural (e.g. volcanism) and anthropogenic origin. Crustally-derived trace metals are generally encountered in the "coarse " (>2.5μ) size fraction, and are largely subjected to dry deposition near the source. Under unique conditions, however, aeolian transport of resuspended soil can occur over long (1000's of km) distances (Duce et al. 1980, Prospero 1987). During high temperature combustion processes, trace metal oxides are vaporized and consequently condense on or form fine sub-micron aerosols (Smith et al. 1979, Natusch et al. 1974). Thus, most atmospheric trace metals are present in association with particles, although some (e.g. Hg and Se) may exhibit significant vapor-phase sources.

Such particulate metals are subsequently entrained in precipitation via two processes: (1) in-cloud nucleation, and (2) below-cloud scavenging by falling hydrometeors. Depending on the associated precipitation chemistry, particulate phases are solubilized to varying degrees before, during or after deposition. Thus, in terms of evaluating deposition, the total wet atmospheric flux of trace metals includes both dissolved and particulate forms. However, from an ecological perspective, the dissolved component is of most interest as it is the most readily available.

Based on a review of recent data reported at worldwide locations (Nguyen et al. 1979, Nurnberg et al. 1984, Gatz and Chu 1986, Lim and Jickells 1990, this work), the phase distribution of trace metals in precipitation appears to be highly variable. In general, the solubility is dependent on the element, the ambient pH, and the chemical properties of the parent aerosol which has been scavenged. For example, these data indicate that under ambient pH, mineral aerosols such as Al are generally insoluble (< 50%), while high temperature combustion condensates such as Pb are highly (>80%) soluble. Furthermore, the prescribed sample acidification will post-depositionally solubilize many elements, although this acid-leachable fraction may underestimate the total concentration of some mineral elements bound in crustal lattices (Lim and Jickells 1990).

Recent experiments in our laboratory support this observation. Filtration (0.2 μ pore size, acid-washed Nuclepore^{R}) of freshly-collected, acidified rainwater samples removed an average of 54% of the "GFAA-analyzable" Fe; in contrast, filtration removed less than 5% of the Zn. Furthermore, a comparison of GFAA with ICP analysis of unfiltered samples (Fig. 2a) indicates that about 1/2 of the total Fe is not detected by GFAA techniques. Even the filtered samples (Fig. 2b) exhibit an apparent underestimation (ca. 40%) by GFAA. (Similar results at both ICP analytical wavelengths insures that this difference is not due to a matrix effect or spectral interference). For both filtered and unfiltered samples, the discrepancy appears to be non-linear, i.e. is proportionately larger at higher Fe concentrations.

Conversely, for Zn we observe excellent agreement between analytical methods for both filtered and unfiltered treatments (Figs. 2c and 2d). Presumably, the Fe phase not detected by GFAA is a refractory micro-colloidal form (probably of local crustal origin) which is detected by ICP due to: (a) higher atomization temperatures in the ICP plasma (6000°C) compared with the GFAA furnace (2500°C) and/or (b) the settling of particles which results in sample heterogeneity. This

effect is largely compensated for by ICP methodology (where the analyte is continuously aspirated) than for GFAA (where a small volume of analyte is discretely sampled). Thus, for some elements, analysis by ICP appears to more accurately reflect the total (wet and particulate) wet depositional flux.

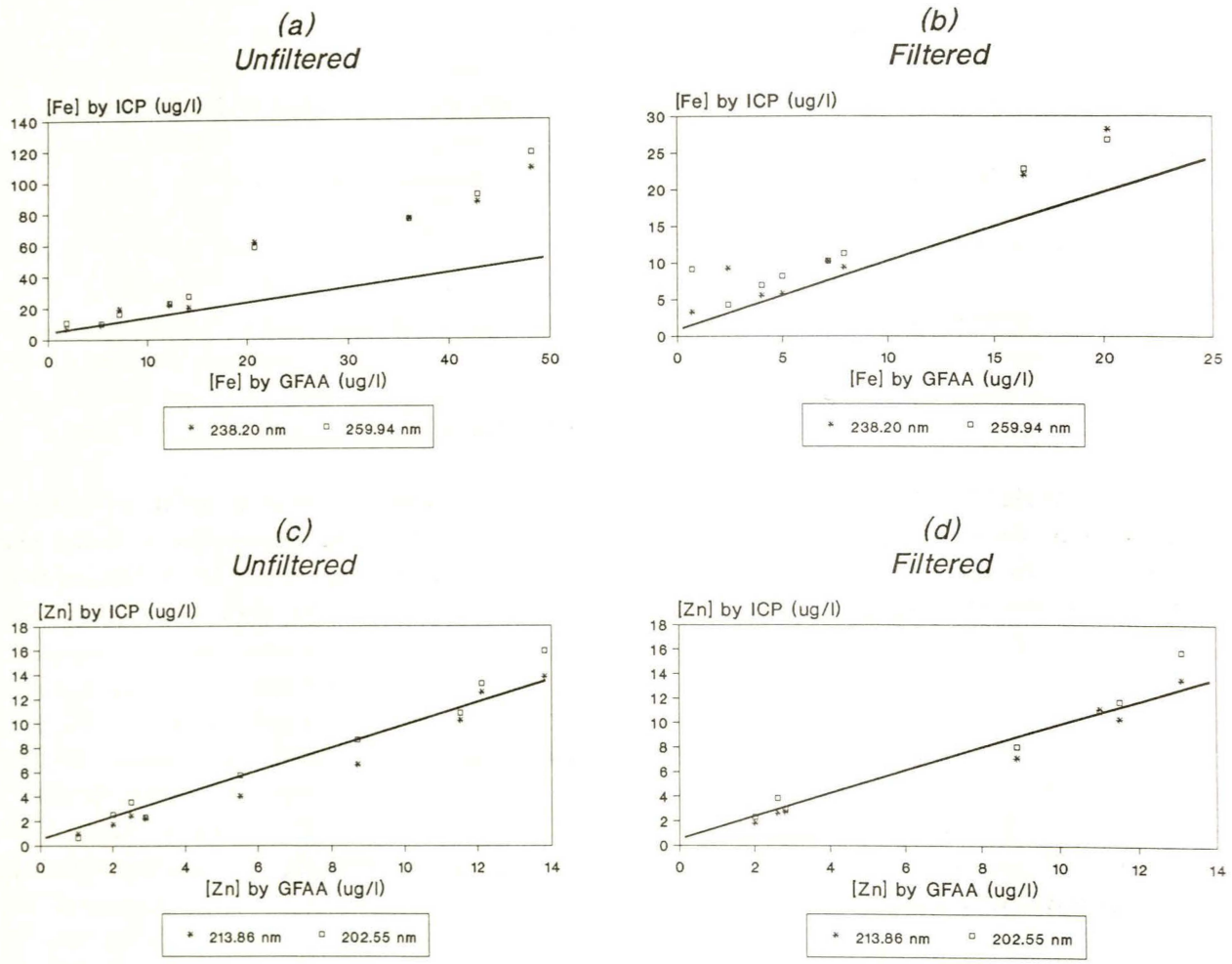

Figure 2.--Acomparison of Fe and Zn concentrations (µg L^{-1}) in filtered and unfiltered precipitation at Lewes, DE, analyzed by GFAA vs. ICP-AES. The line is a 1:1 correlation.

CONCLUSIONS

According to the procedures reported in this paper, the accurate determination of the total (dissolved and particulate) trace metals concentration in precipitation is accomplished by:

(1) meticulous sample handling and processing procedures;

(2) exclusive use of acid-washed plasticware;

(3) utilizing a modified ACM collector equipped with HDPE collection bucket;

(4) sample acidification with ultra-high parity acid (HNO_3 or HCl);

(5) analysis by GFAA and ICP;

(6) strict adherance to a QA/QC program.

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A PILOT NETWORK FOR THE COLLECTION AND ANALYSIS OF METALS IN WET DEPOSITION

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ABSTRACT.--A pilot network of three sites was initiated to test the feasibility of quantifying metals in wet deposition, and to make recommendations for a sub-network at a level compatible with existing NADP/NTN sites. Modifications were made to Aerochem Metrics samplers, incorporating all Teflon^R surfaces. Preliminary results show that inductively coupled plasma mass spectrometry (ICP-MS) is well adapted to the routine analysis of As, Cd, Cu, Mn, Pb and Zn in precipitation, as is cold vapor atomic fluorescence spectroscopy (CVAFS) for Hg, at the low $\mu g\ L^{-1}$ and $ng\ L^{-1}$ level, respectively. Results also demonstrate our ability to measure metal concentrations in precipitation without introducing significant contamination. The Teflon^R used in this study (fluorinated ethylene propylene - FEP), given current treatment methods, strongly adsorbed Hg. Pre-baked borosilicate glass proved to be a better sampling container for Hg under these conditions.

INTRODUCTION

Metals in precipitation may constitute an important stress on aquatic and terrestrial systems and the measurement of their deposition could be critical to our understanding of geochemical cycling and the impacts on both terrestrial and aquatic ecosystems (Hutchinson and Meema 1987). The natural biogeochemical cycles of many metals have been drastically altered by the activities of man (Galloway et al. 1982), and `atmophile' metals (e.g. As, Cd, Cu, Hg, and Zn) -- having the atmosphere as their major media for transport in the biosphere -- are readily removed by wet deposition.

Available data on trace metals in wet deposition have been collected using a wide variety of collection devices, employing various handling procedures and different analytical techniques. A lack of standardization of sampling and analysis protocols hampers comparisons among different

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published works (Tri-Academy 1985). Furthermore, Barrie et al. (1987) have cast a shadow over old metal data (pre-1982), pointing out that many values reported previously in the literature may be in error due to contamination.

The major chemical deposition monitoring networks (e.g. NADP/NTN and MAP3S) measure only pH and major ions (eg. Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, SO_4^{2-}, NO_3^{-} and Cl^{-}) in wet deposition. A national network for the monitoring of metals in wet deposition does not exist in this country, although recommendations for such a network and for standardization of sampling and analysis protocols have come from a number of sources (Galloway et al., 1982; American Society for Testing and Materials -- Campbell (1983), NAPAP (1984), Tri-Academy (1985).

The work reported in this paper describes our efforts to establish a pilot network for metals in precipitation that is compatible with the larger NADP/NTN network. This includes development and evaluation of protocols for: 1) collection devices; 2) sample handling (field and laboratory); 3) chemical analysis; and 4) operator training. The pilot network was designed at two levels: 1) network operation, based on perceived `best methods'; and 2) evaluation of a number of alternative designs and protocols. An illustration of using `best methods' is the exclusive use of Teflon^R surfaces and bottles for sample collection and storage. Teflon^R has been shown to contain low levels of metals and is a preferred material for storage containers, especially recommended for Hg and Zn (Fogg and Fitzgerald 1979). At the conclusion of one year of sampling, recommendations are to be made regarding the implementation of a national network. Results presented in this paper are considered preliminary, and include only the Spring/Summer 1991 season.

EXPERIMENTAL DESIGN

The network was started in the spring of 1991 at three locations: Arvada, CO (CO01), Champaign, IL (IL01) and Oak Ridge, TN (TN01). The network samplers operate at all three sites, with CO01 and IL01 additionally serving as sites to evaluate alternative sampling and processing methods. A schematic of the network design is illustrated in Figure 1.

SAMPLER MODIFICATIONS

Modifications to the Aerochem Metric Sampler (Model 301), as used throughout the NADP/NTN network, involved two different designs. Common to both designs is the use of Teflon^R coated funnels and Teflon^R tubing connecting the funnel to a 2L or 5L Teflon^R bottle such that collected precipitation contacts only Teflon^R surfaces. Modifications to the network sampler (hereafter referred to as sampler 'A') features a Teflon^R coated aluminum collection funnel, held in place by a vented aluminum housing (Figure 2). The collector lid arms are Teflon^R coated and the metal collector lid and pad are replaced with a polyethylene lid and Teflon^R fabric pad. The bottom of the sampler is enclosed in aluminum and insulated with Celotex Tuff-R. Within the enclosure a thermostat activates either a cooling fan (incoming air passed through a filter) or heater. Exposure of the funnel to the heated enclosure allows for the melting of collected snow.

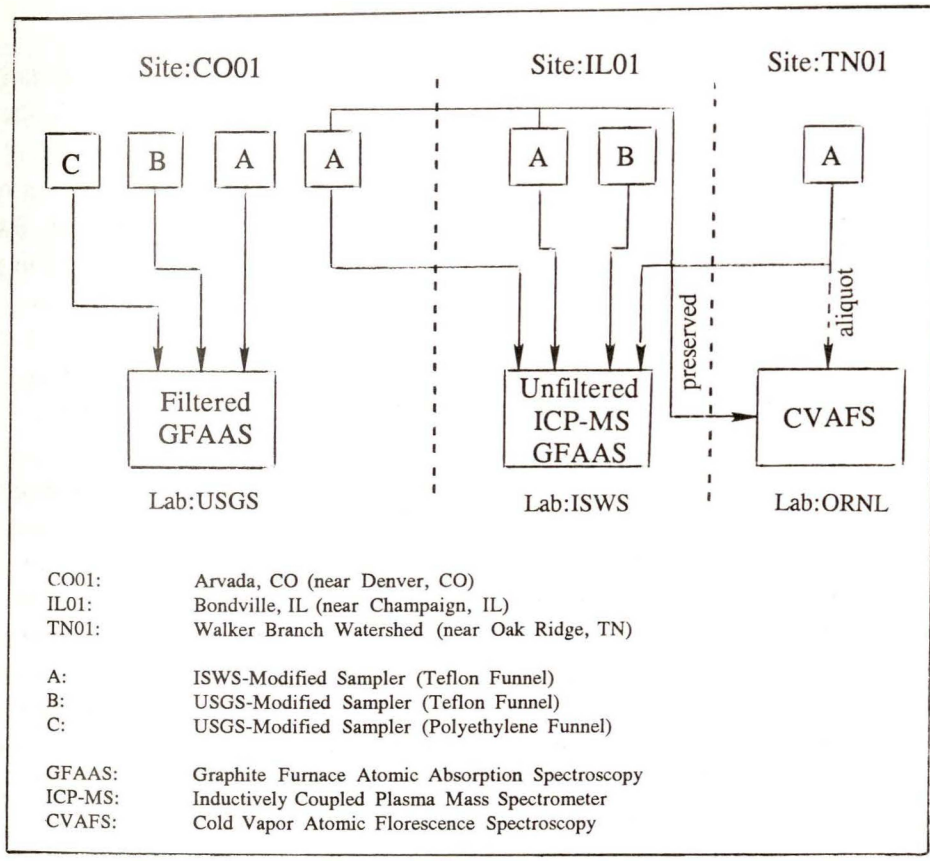

Figure 1.--Flow diagram showing pilot network sampling and analysis protocol.

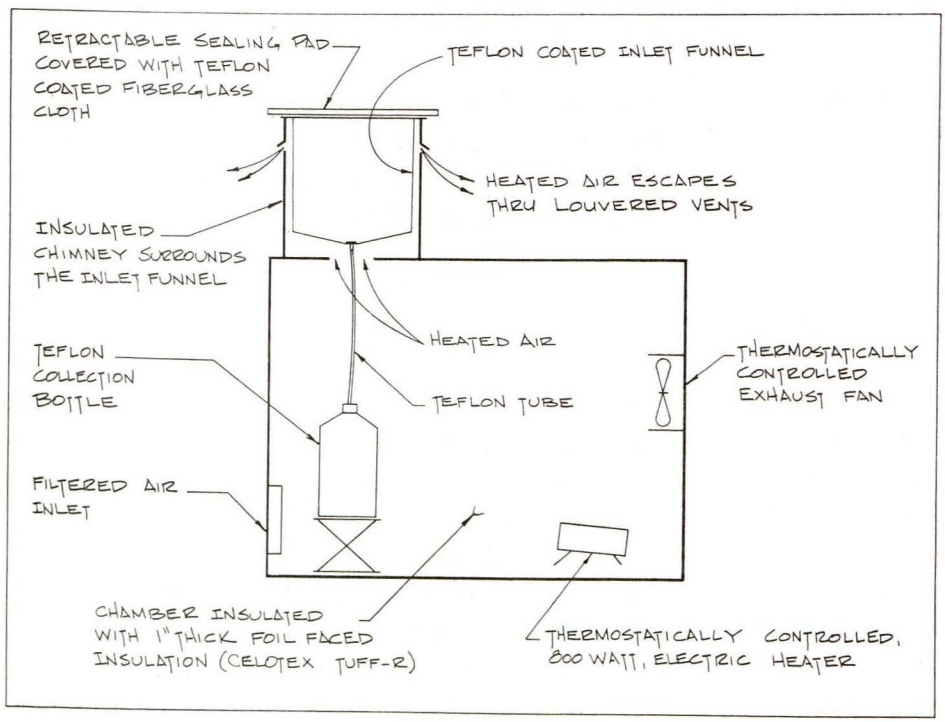
RETRACTABLE SEALING PAD COVERED WITH TEFLON COATED FIBERGLASS CLOTH
TEFLON COATED INLET FUNNEL
HEATED AIR ESCAPES THRU LOUVERED VENTS
INSULATED CHIMNEY SURROUNDS THE INLET FUNNEL
HEATED AIR
TEFLON COLLECTION BOTTLE
TEFLON TUBE
THERMOSTATICALLY CONTROLLED EXHAUST FAN
FILTERED AIR INLET
CHAMBER INSULATED WITH 1" THICK FOIL FACED INSULATION (CELOTEX TUFF-R)
THERMOSTATICALLY CONTROLLED, 800 WATT, ELECTRIC HEATER

Figure 2.--Schematic of modifications to sampler 'A'

Modifications to an alternative sampler (sampler 'B') include a Teflon^R coated stainless steel collection funnel, held in place by the standard NADP/NTN collection bucket. The collector frame, collector lid arms and collector lid are covered with an adhesive backed Teflon^R sheeting. The bottom of the sampler is enclosed with aluminum and not insulated. For a third sampler (sampler 'C') the teflon^R coated funnel was replaced with a polyethylene funnel. Each of the samplers was activated by the sensor mechanism of the NADP/NTN sampler at the respective sites.

SELECTED METALS AND PRESERVATION PROTOCOLS

The metals chosen for study were As, Cd, Cu, Hg, Mn, Pb and Zn, based on the importance of anthropogenic inputs, geochemical mobility, toxicity, and potential for bioaccumulation. A review of previous studies provided a consensus for the seven metals (i.e. Galloway et al. 1982, Tri-Academy 1985). The core network was limited to the analysis of "acid extractable" metals -- defined as the amount of dissolved plus particulate metals released to solution following 24 hour equilibration with dilute acid (0.2% v/v ultrapure HNO_3). The "acid extractable" metal would then represent an estimate of the maximum biologically available metal concentration. An alternative method that was evaluated was the filtration of the sample, using an all Teflon^R filtration unit, after equilibration with the same concentration of dilute acid for the purpose of removing particles from the analytical sampling stream.

SAMPLING PROTOCOL

As illustrated in Figure 1, weekly samples (Tuesday to Tuesday) from all three sites were shipped from sampler 'A' (in the original collection bottle) to the ISWS laboratory for acidification (unfiltered) and elemental analysis. An acidified aliquot was then shipped to the ORNL laboratory for Hg analysis. The collection bottles and funnel assemblies for sampler A were cleaned and shipped to the sites from the ISWS laboratory. Briefly, cleaning procedures included a series of rinses or soaks in alternating DI water and 10% reagent HNO_3. Neither cleaning nor sample handling was conducted in a class 100 clean room. Precipitation samples from sampler 'B' at the IL01 site were treated in a similar fashion. For the CO01 site, precipitation samples from the second 'A' sampler and from samplers 'B' and 'C' were acidified with HNO_3 prior to filtration and analyzed at the USGS laboratory. Collection bottles and funnel assemblies were cleaned as per the ISWS methods.

ANALYTICAL METHODS

The wet deposition samples for the ISWS laboratory were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS) and graphite furnace atomic absorption spectrophotometry (GFAAS) -- the latter was used as a quality assurance check. GFAAS was used at the USGS laboratory as the principle method of analysis. Mercury was analyzed using dual-trap cold vapor atomic fluorescence spectroscopy (CVAFS) at ORNL (Fitzgerald and Gill 1979).

The low level of the metal analytes dictated that the samples and all standards be treated with the utmost concern for contamination. The ICP-MS methodology is described in more detail. The wet deposition samples were subsampled by using a micropipet, transferring 10 mL to a cleaned polypropylene tube. Standards were also made by transferring the appropriate amount of stock standard and ASTM Type 1 water to cleaned polypropylene tubes. Both samples and standards were spiked with an internal standard (100 $\mu g\ L^{-1}$ of molybdenum and thallium). These elements were chosen because of their mass proximity to the analytes of interest and their absence from the samples themselves. The internal standards account for any drift in sensitivity of the ICP-MS instrument. Standards were made in the range of 0.1 $\mu g\ L^{-1}$ to 10 $\mu g\ L^{-1}$. Standards and samples were analyzed by the ICP-MS instrument by integrating the signal at the peak of each mass for 3000 msec. The long integration time is required at these concentration ranges to assure good precision and accuracy. All the calibration curves were inspected for linearity before any samples were analyzed.

Quality control standards used were certified at levels comparable to the precipitation samples (Table 1).

Table 1.--Certified Concentrations of Quality Control Standards.

Element	SLRS-1[1] ($\mu g\ L^{-1}$)	WS378[2] ($\mu g\ L^{-1}$)	ICAP-19[3] ($\mu g\ L^{-1}$)
As	0.55	0.25	2
Cd	0.015	0.026	2
Cu	3.58	n.a.	2
Hg	n.a.	0.016	2
Mn	1.77	n.a.	2
Pb	0.106	0.26	2
Zn	1.34	n.a.	2

[1]National Research Council of Canada Riverine Water Reference Material For Trace Metals
[2]USEPA Water Supply Quality Control Samples (WS378 Con. 4, diluted x100)
[3]USEPA Quality Control Sample ICAP-19 (lot no. WP988, diluted x500)

RESULTS AND DISCUSSION

Results presented in this paper are for 15 weeks of sampling, from 16 April 1991 to 20 August 1991 (results for Hg extend to 3 September 1991). A summary of volume-weighted mean concentrations for each of the network sites is presented in Table 2. Results are comparable to selected sites from the Great Lakes Atmospheric Deposition (GLAD) network and to selected works in the literature.

Table 2.--Network volume-weighted means and comparisons with other studies.

Site	As[1] µg L^{-1}	Cd[1] µg L^{-1}	Cu µg L^{-1}	Hg µg L^{-1}	Mn µg L^{-1}	Pb µg L^{-1}	Zn µg L^{-1}
All Samples							
CO01[2]	0.15	0.07	0.99	0.0028	5.67	1.36	3.91
IL01[2]	0.09	0.10	0.59	0.0017	2.17	0.98	2.00
TN01[2]	0.12	0.24	0.72	0.0016	1.45	0.86	1.97
Excluding Overflow Samples							
CO01[2]	0.15	0.09	1.32	0.0028	6.57	1.49	4.05
IL01[2]	0.10	0.12	1.33	0.0017	3.48	1.11	3.06
TN01[2]	0.19	0.34	0.69	0.0013	2.13	0.87	2.86
Literature Values							
GLAD[3]	n.a	0.2	1.0	n.a.	n.a.	1.7	8.7
Rural[4]	0.24	0.05	0.45	0.025	n.a.	1.4	0.8
Urban[4]	0.9	0.35	2.8	0.065	n.a.	6.0	3.5

[1] Samples analyzed using automatic sampler are excluded (see text).
[2] Pilot network determinations from ICP-MS and CVAFS (Hg).
[3] GLAD network - 1987/Rural/Lake Michigan - Klappenbach (personal communication)
[4] Compiled from recent literature (Nriagu, 1992)

The numerous variations in sampler design, funnel types, cleaning procedures, analysis of "acid extractable" aliquots with and without filtration, participating laboratories, etc., within the project provide a number of useful comparisons that can be used to select the "method of choice" for network implementation. A number of the more salient points are addressed in this paper, especially as related to the feasibility of monitoring metals in wet deposition on a routine network basis.

PERFORMANCE OF SAMPLERS AND ANALYTICAL SYSTEMS

The modified samplers have performed well over the reported period, however the use of 2 L collection bottles resulted in a number of sampling overflows (e.g. when weekly rainfall totals exceeded 3 cm: CO01-33%; IL01-25%; TN01-60% of the samples collected). Five liter collection bottles have recently been introduced to the network and are presently in use at the TN01 site.

The ICP-MS system is well adapted for the measurement of As, Cd, Cu, Mn, Pb and Zn at the sub μg L^{-1} level, and with only 10 mL of sample. For many of the samples the concentrations were below the detection limit of GFAAS (Table 3). Where above detection, GFAAS and ICP-MS compared well between paired samples (for Cu $R^2 = 0.99$, Slope = 0.89; Mn $R^2 = 0.99$, Slope = 0.99; Pb $R^2 = 0.92$, Slope = 0.91; Zn $R^2 = 0.89$, Slope = 0.53). Use of an automatic sampler was discontinued after giving suspect values for standards and samples, especially for As and Cd. The CVAFS system is well adapted to routine analysis of Hg in rain at the ng L^{-1} level. Mercury can readily be detected in samples as small as 60 mL, and probably in samples of 20-30 mL with a new bubbler apparatus now being assembled -- the limiting factor being blank levels.

Table 3.--Detection limits and the percent of metal determinations reported above detection for GFAAS and ICP-MS[1].

	Detection Limit (μg L^{-1})				Precipitation Samples Above Detection Limit (%)			
Metal	GFASS (USGS)	GFAAS (ISWS)	ICP-MS (ISWS)	CVAFS (ORNL)	GFAAS (USGS) N=12	GFAAS (ISWS) N=9	ICP-MS (ISWS) N=34	CVAFS (ORNL) N=16
As	1.0	0.80	0.02	--	0	0	94	--
Cd	0.1	0.03	0.007	--	33	56	97	--
Cu	0.5	0.43	0.009	--	100	67	100	--
Hg	--	--	--	0.001	--	--	--	100
Mn	0.2	0.13	0.001	--	100	100	100	--
Pb	0.5	0.41	0.02	--	50	78	100	--
Zn	0.5	0.10	0.006	--	67	100	97	--

[1]GFAAS = Graphite Furnace Atomic Absorption Spectrophotometry, ICP-MS = Inductively Coupled Plasma Mass Spectrophotometer, USGS = United States Gelogical Survey, ISWS = Illinois State Water Survey, and ORNL = Oak Ridge National Laboratory.

FEASIBILITY OF METAL QUANTIFICATION

Minimizing contamination, such that blank concentrations are well below natural precipitation, is critical to the establishment of a wet deposition trace metal monitoring network. A summary of quality assurance blanks is presented in Figure 3. We evaluated the quality of acidified DI water, residual contamination from Teflon^{R} bottle cleaning (reused bottle), residual contamination from the funnel assembly (lab rinse), contamination from the polyethylene bags which the funnels are sealed in during shipping (shipping bag), contamination from the funnel assembly after installation in the field (field rinse), and passive contamination of the funnel assembly after installation in the field for one week (system blank). Overall, the DI water, bottles, and funnel assembly are not significant sources of metal contamination. However, the polyethylene bags, in which the funnel assemblies are shipped, may be a source of Cd and Zn contamination. Although precipitation samples are not collected in the polyethylene bags, some contamination of the funnel may result from contact between a wet funnel and the bag. Blank contamination was most significant for the field rinse. The contamination appears random between elements, suggesting the short exposure to the air during funnel set up as a possible contamination source. With sampler 'B', the funnel assembly was rinsed with 2 L of DI water prior to pouring in the funnel rinse. This `pre-rinse' of the funnel reduced the contamination.

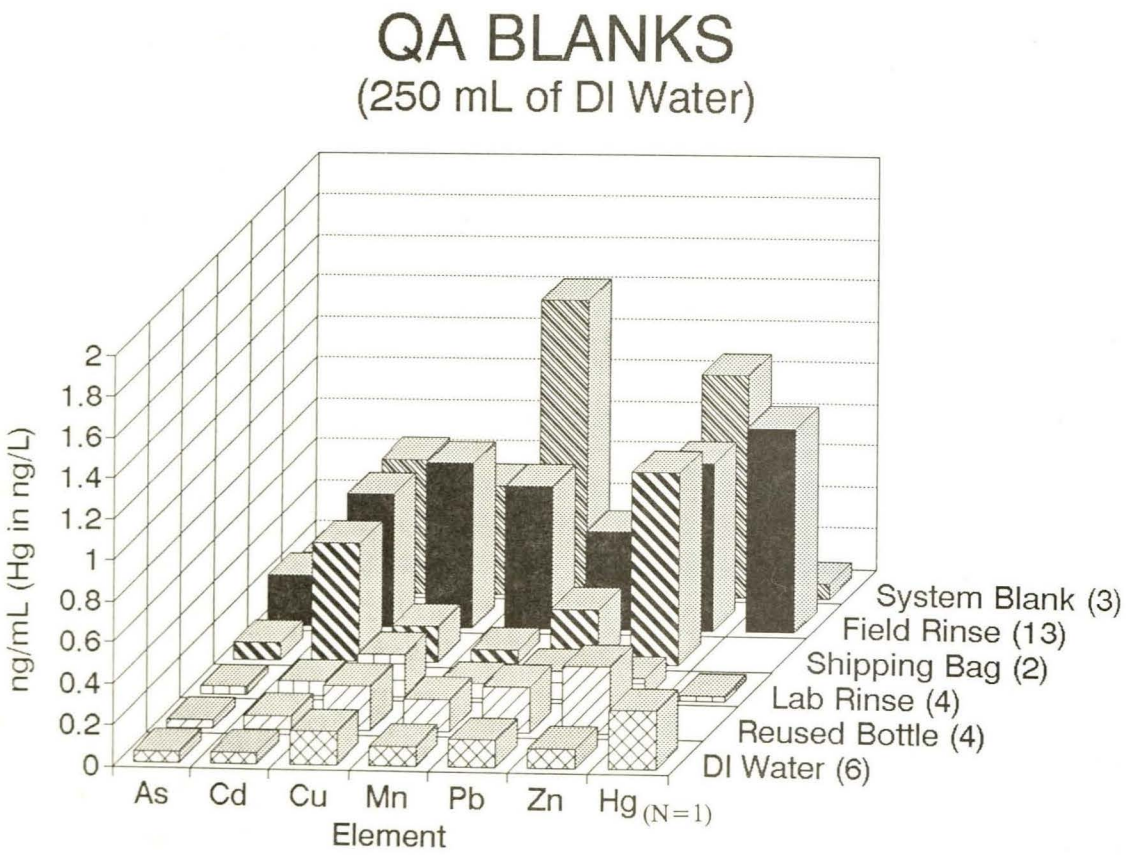

Figure 3.--Laboratory and field quality assurance blanks for sampler 'A'. Values in parentheses are sample sizes.

Success in quantifying metal concentrations in actual samples above those of field rinses is illustrated in Table 4. Metal concentrations in precipitation are significantly above field rinse values.

Table 4.--Field rinse and rain sample mass (µg) collected during corresponding weeks.

Element	N	Field Rinse (mean±S.D.)	Rain Sample (mean±S.D.)
As[1]	7	0.006±0.002	0.05±0.03
Cd[1]	7	0.01±0.008	0.13±0.16
Cu	14	0.18±0.14	0.78±0.72
Hg[2]	16	0.00025	0.0024±0.0026
Mn	14	0.15±0.15	4.08±5.06
Pb	14	0.10±0.10	1.26±1.10
Zn	14	0.23±0.19	2.75±1.90

[1]Samples analyzed using the automatic sampler are excluded.
[2]Contrasting a single field rinse to all Hg rain samples.

MERCURY LOSSES WITH TEFLON^R

The Hg levels reported in Table 1 are comparable across the network but are at the low end of the literature range. A number of our experiments suggest that these values are low due to adsorption of Hg onto walls of the Teflon^R sampling bottle. For example, the mean Hg in 5 paired event (collected in pre-baked borosilicate glass bottles) and weekly samples at TN01 (collected in Teflon^R) was 16 ng L^{-1} versus 2.2 ng L^{-1}, respectively. As shown in Figure 4, glass appears to be a better sampling container for analysis of Hg in precipitation based on a comparison of event samples collected in glass versus our standard Teflon^R containers (fluorinated ethylene propylene-FEP), and based on spike recovery tests. Interestingly, both the acidified and unacidified splits suggest that Hg losses in Teflon^R occur after shipping and not during storage in the field during the week of sampling. Discussions with other Hg experts indicate that new Teflon^R bottles have previously been found to adsorb Hg unless they are more severely "pre-treated" and "conditioned" than were the bottles prepared in this study (e.g. extended boiling in concentrated acids, R. Mason, University of Connecticut, personal communication). We are pursuing this procedure at present.

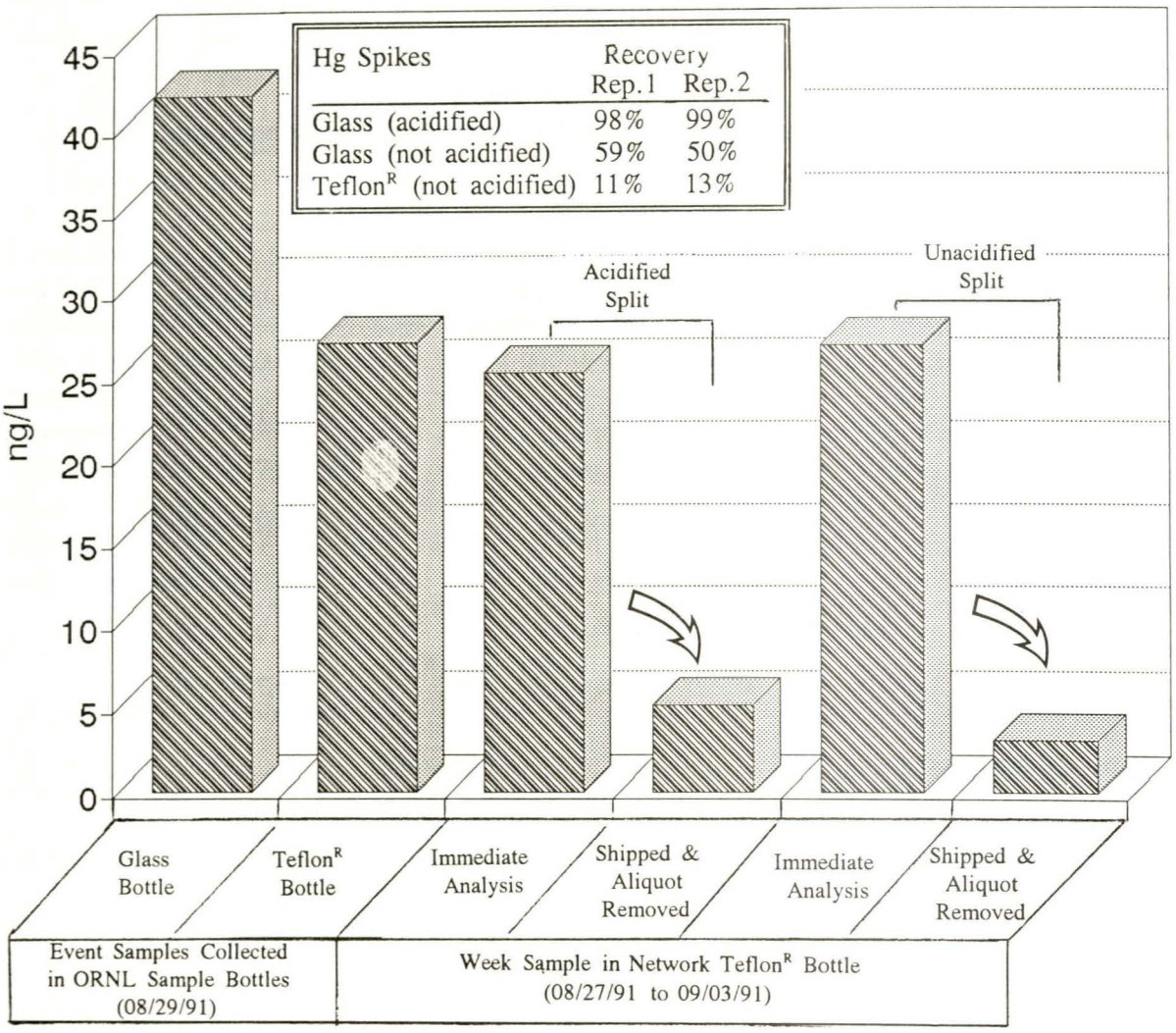

Figure 4.--Mercury losses in Teflon[R] as illustrated in one "paired" experiment at TN01. The bar at the far right represents the normal pilot network sample.

COMPARISON OF FUNNEL AND SAMPLERS

As previously noted, it is premature to evaluate the many alternative protocols, designs and materials studied within this project, however, results of two comparisons can be mentioned at this time. First, a comparison of Teflon[R] versus polyethylene funnels has shown no substantial difference in metal concentrations in the collected precipitation for As, Cd, Cu, Mn, and Pb.

However, there is a hint of Zn contamination coming from the polyethylene funnel (Hg was not evaluated). Second, a comparison of samplers 'A' and 'B' show comparable concentrations for each metal, with the exception of Mn (Hg was not evaluated). Sampler 'B', using a Teflon^R coated stainless steel funnel, exhibited higher Mn values (a median of 6 ng mL^{-1} compared to 2 ng mL^{-1}) in collected precipitation samples. The discrepancy is thought to be contamination from the stainless steel.

CONCLUSIONS

Network operation has continued beyond the 15 weeks of sampling reported in this paper, and will continue through the winter of 1991-1992. At the conclusion of this project recommendations will be made on the feasibility of implementing a larger-scale network at site and training levels compatible with many NADP/NTN sites. Based on the sampling and analytical work to date, the following conclusions/recommendations can be made:

1. The metals As, Cu, Hg, Mn, Pb and Zn can be accurately quantified in precipitation within practical constraints of network sampling.

2. ICP-MS is well adapted to routine analysis of As, Cd, Cu, Mn, Pb and Zn in precipitation at the low ng mL^{-1} level, and generally out-performed GFAAS with respects to levels of detection (i.e. As and Cd). CVAFS is well adapted to routine analysis of Hg in precipitation at the ng L^{-1} level.

3. The Teflon^R bottles used in this study strongly adsorb Hg from precipitation samples and pre-baked borosilicate glass bottles seem a better sampling container based on current methods of bottle preparation.

4. Comparisons between Teflon^R and polyethylene funnels show no significant difference in adsorption or contamination of the precipitation sample, with the possible exception of Zn.

5. Comparisons between Teflon^R samplers (A and B) shows no real differences in metal levels, with the exception of Mn contamination in samples and field rinses for sampler 'B' (using a Teflon^R-coated stainless steel funnel).

ACKNOWLEDGEMENTS

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PALEOLIMNOLOGICAL EVIDENCE OF METAL POLLUTION FROM ATMOSPHERIC DEPOSITION

Stephen A. Norton and Jeffrey S. Kahl [1]

High quality time series data on the concentrations of metals in atmospheric deposition are rare. In lieu of such data, dated chemical stratigraphies in lake sediments and in peat from bogs can be used to infer trends in atmospheric deposition. The absolute amount of material deposited from the atmosphere is difficult to infer, due to watershed and in-lake processes that may either increase or decrease the net accumulation rate. The method is best suited to metals such as Pb, with low mobility under normal environmental conditions.

INTRODUCTION

A wide variety of human activities has resulted in increased emissions of trace metals to the atmosphere and thus increased deposition to the earth's surface. These activities include the burning of fossil fuels, smelting, metal finishing, glass making, and agricultural practices. In this paper, we focus on the air pollution record for the United States, a history of air pollution that extends to, at least, the mid-1800's. There is a lack of historic data of high quality for trace metals in wet deposition or in air prior to 1980 (Galloway et al. 1982). Furthermore, those studies that have been conducted were limited spatially and temporally. Consequently, paleolimnological studies have been undertaken to determine:

1. What are the pollution histories of various metals and how do they vary spatially?
2. Is it possible to identify specific sources for metals?
3. How faithfully do sediments record trends in emission and deposition rates?
4. How faithfully do sediments record absolute values for atmospheric deposition, and the corollary - how well are integrated depositions recorded?
5. How representative is a single core from a lake or peat bog?

The trace metals for which anthropogenic atmospheric emissions have resulted in elevated regional deposition include As, Be, Cd, Cu, Hg, Ni, Pb, V, and Zn (see Norton and Kahl 1991 for references). Here we focus on Pb because of the frequency with which it has been studied and the quality of records.

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METHODS

The basic premises of using sediments (and peat) for the study of air pollution is that 1) accumulation of sediment is more or less continuous and 2) some fraction of the atmospheric metal accumulates in sediment shortly after deposition. Lake sediment cores are typically retrieved from the deeper part of the basin where accumulation rates of fine-grained sediment are highest and more continuous. Corers are typically of the piston type (e.g., Davis and Doyle 1969) which retrieve undisturbed sediment. Peat from ombrotrophic bogs is typically cored with stainless steel tubes with serated teeth on one end. Compression of sediment is not a problem in such conditions. Lakes and bogs selected for study are free from point-source pollution within the catchment and have undisturbed watersheds.

Dating and chemical analysis of sediment and peat cores establishes *when* events occurred and *how much* material was deposited per unit area per unit time. Sediments are dated using varves (Simola 1977) or the naturally occurring radionuclide ^{210}Pb, which has a half life of 22 years (Appleby et al. 1986). These techniques may be used to develop secondary continuous age-depth relationships such as the relative abundance of soot particles (Wik and Renberg 1991). Checks on the accuracy of the varve or ^{210}Pb dates are provided by chrono-stratigraphic markers such as pollen changes, ^{137}Cs and ^{241}Am peaks (Appleby et al. 1991), magnetic spherules (McLean 1991), and other chemical variables with known input functions.

Methods of sediment preparation for chemical analysis are highly variable and yield information that is unique to the method. For example, White and Gubala (1989) analyzed successive extractions of progressively less labile components of metals to demonstrate changes in the state and amount in which metals are deposited. Many studies report acid-extractable fractions of metals. We have analyzed for the total amount of metal in sediment (bulk) (after Buckley and Cranston 1971).

Primary data for sediment cores typically includes: depth interval, water content, oxidizable hydrocarbon content, radionuclide activity (pCi g^{-1} dry sediment) and concentrations of various metals (g g-1 dry weight or ashed weight). Data may be presented as: concentration, enrichment factor, total accumulation rate, accumulation rate of a certain analytical fraction, or and "anthropogenic" fraction of the total accumulation rate. These values are typically plotted versus depth of sediment, age of sediment (years), or calendar time.

APPLICATIONS

SINGLE-LAKE, SMALL REGION APPLICATIONS

Figure 1A depicts concentrations and manipulated data for a sediment core taken from Deep Lake, Adirondack Mountains, NY. Prior to 1850, the concentration of Pb in the sediment was relatively constant - near 25 parts per million (ppm). The concentration increased to a maximum near 775 ppm about 1975 and thereafter decreased to 265 ppm by 1984. The timing of this decline coincides with a decline in the use of leaded gasoline in the United States and the noted decline of Pb in air (Eisenreich et al. 1986). The timing and trends for virtually all lakes in the eastern United States are very similar to this profile. The exception is that the near-recent decline is less pronounced or even absent at some lakes. Background concentrations of Pb and sediment accumulation rates (mg cm^{-1} yr^{-1}) vary from lake to lake and thus enrichment factors (total Pb/background [pre-1850] Pb) (Fig. 1A) among lakes vary accordingly (not shown). Enrichment factors may range over an order of magnitude in the same air-shed, due to variations of in-lake sediment processing.

The accumulation rate of *total* Pb (ΣPb) (μg cm^{-2} yr^{-1}) roughly parallels the trend of the concentration profile (ppm) at Deep Lake (Fig. 1A). However, this need not occur in all lake cores because atmospheric loading of Pb is independent of the sedimentation rate. This occurs because the total Pb accumulation rate (ΣPb) derives from two components: Pb derived directly or indirectly (via dust) from the catchment soils and rocks (Pb_b), and Pb derived directly or indirectly (via the watershed) from anthropogenic additions to the atmosphere ($Pb_{an.}$). The atmospheric component of the total Pb (or anthropogenic component; Fig. 1 A,B) has been calculated assuming that a certain fraction of the total Pb is derived from the watershed geologic material. This is proportional to titanium (Ti) deposited in the sediment (Norton and Kahl 1991). Atmospheric Pb ($Pb_{an.}$) dominates total Pb in Deep Lake, as it does for all lakes in the eastern U.S. (Fig. 1A).

Different lakes receiving comparable deposition of atmospheric Pb do not not necessarily record similar accumulation rates. In Adirondack Mountain lakes, the accumulation rates range over an order of magnitude (Fig. 1B). However, the timing of the increases and the trends in accumulation rates of anthropogenic Pb are similar. Similar relationships are found in other lake districts where clusters of lakes have been studied (Norton et al. 1990).

No simple relationship between accumulation rate of Pb and limnological characteristics explains the magnification or minification of the atmospheric signal. However, the integrated anthropogenic Pb (ΣPb_A) within a core segment is strongly related to the rate of sediment accumulation for that core segment (Figure 2A). Ten lakes in the Adirondacks also exhibit a reasonable correlation between the maximum accumulation rate of total Pb or total vanadium (V) and the integrated unsupported activity of ^{210}Pb in the same core (Fig. 2B). The simplest explanation for these relationships is that the accumulation rate of total Pb (and ^{210}Pb) is controlled by sediment focussing.

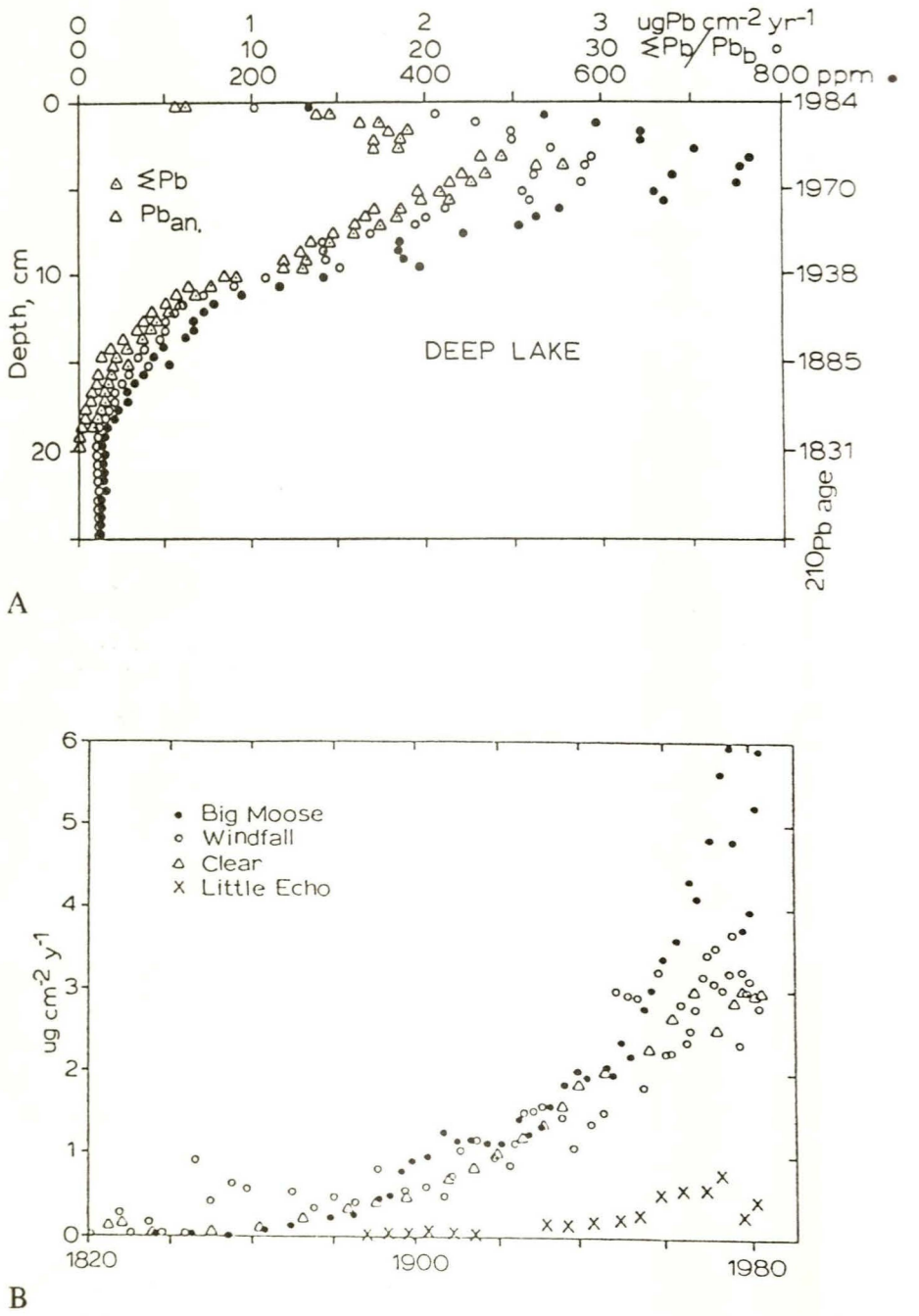
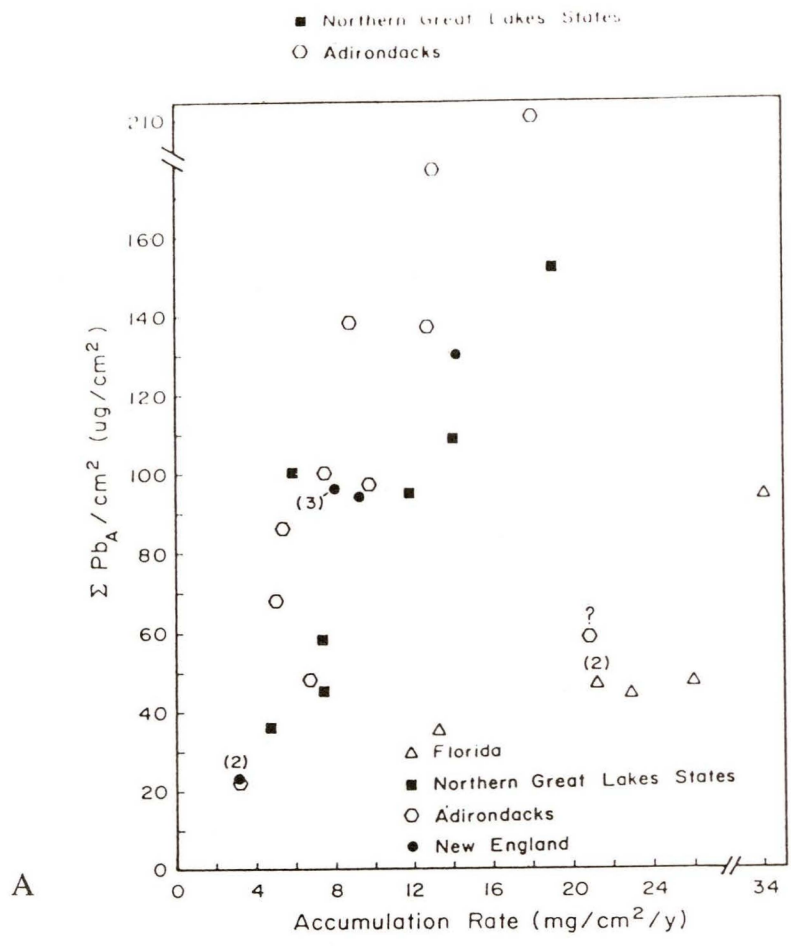


Figure 1. (A) Concentration (ppm), enrichment ratio ($\Sigma Pb/Pb_b$), and accumulation rate ($\mu g\ cm^{-2}\ yr^{-1}$) for total Pb (ΣPb) and anthropogenic Pb ($Pb_{an.}$). (B) Anthropogenic Pb accumulation rate from four lakes in the Adirondack Mountains, NY (from Norton et al. 1990).



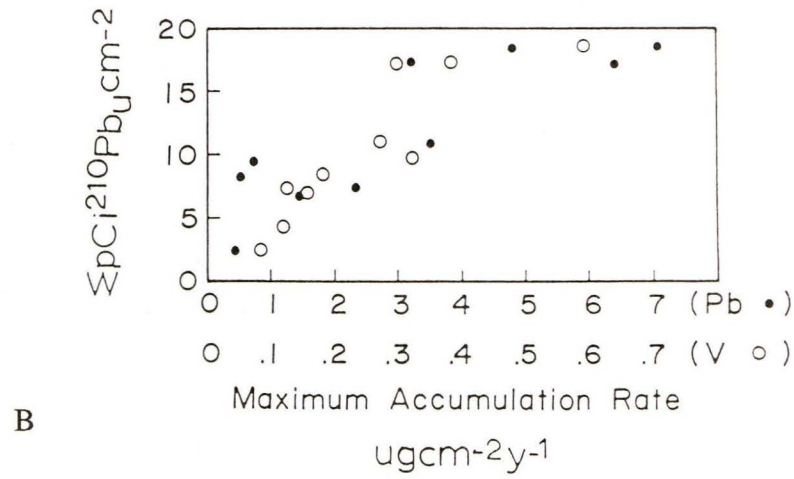


Figure 2. (A) Integral anthropogenic Pb (ΣPb_A) versus sediment accumulation rate from four lake districts, eastern U.S. (B) Integral unsupported ^{210}Pb ($\Sigma pCi^{210}Pb_u$ cm^{-2}) versus maximum accumulation rate for total Pb and total vanadium from 10 Adirondack lakes.

WITH-IN LAKE/BOG VARIATION

The representativeness of a single core has been evaluated in numerous studies. Multiple cores were taken within a few meters of each other in three of the 18 Adirondack Mountain lakes (Fig. 3) and give quite consistent results. Similar results prevail in other lake districts. However, multiple cores taken at different depths in the same lake give a different chronology for changing concentrations, different accumulation rates, and different integral anthropogenic Pb (Fig. 4A). Unsupported ^{210}Pb and sediment accumulation rates are also different (Kahl and Norton 1983).

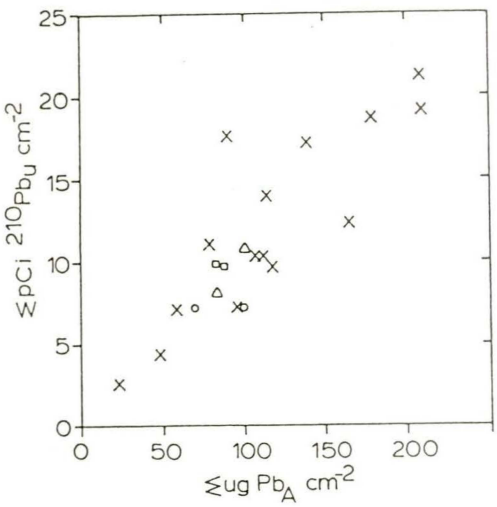
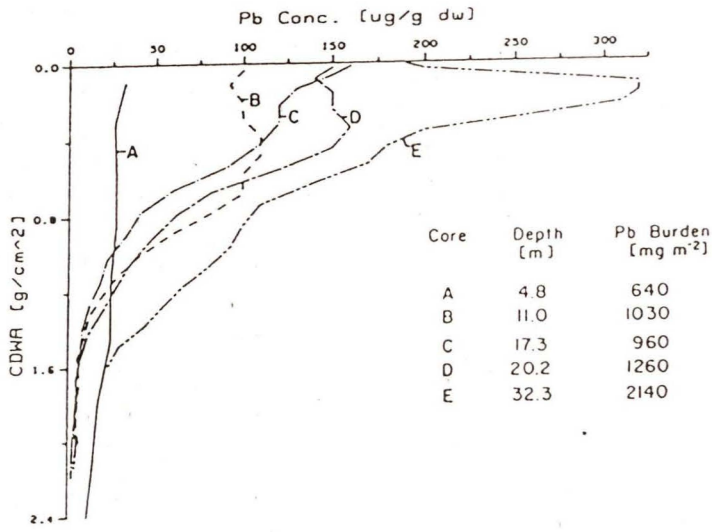
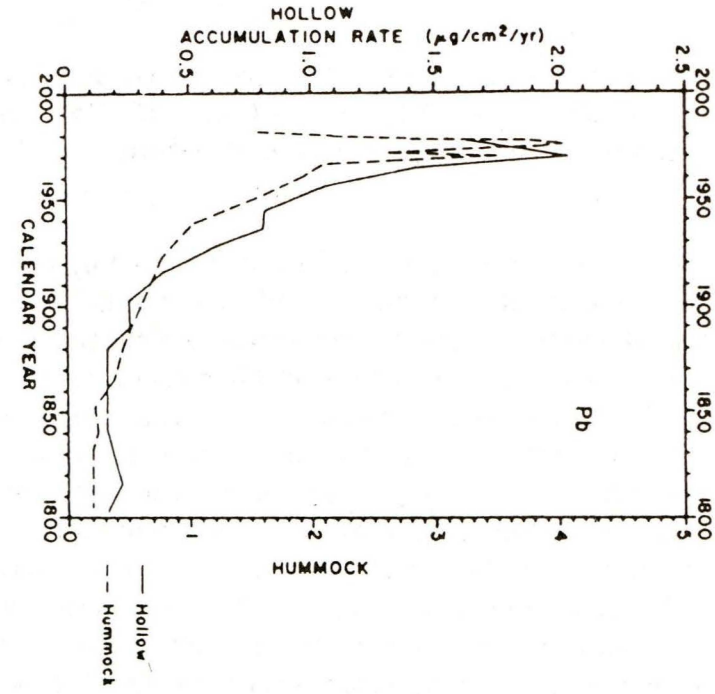


Figure 3. Intergral unsupported ^{210} Pb versus integral anthropogenic Pb for sediment cores from 18 lakes in the Adirondack Mountains, NY. Open symbols indicate different studies at the some lake (from Norton et al. 1990).

Ideally, one would like to have a transfer function relating lake sediment trace metal time-series to air quality or precipitation chemistry. We know of no studies that closely link lake sediment accumulation rates with air quality and precipitation chemistry. In lieu of precipitation chemistry, one approach uses the accumulation rate of Pb in peat cores from ombrotrophic bogs. Such bogs receive all their nutrients from the atmosphere. Thus the accumulated Pb is all atmospheric in origin. However, microtopography within the bog can cause variation of deposition rates. The accumulation rates of total Pb for cores from an adjacent hummock and hollow site at Big Heath, Acadia National Park, Maine show Pb pollution being initiated at least by 1900 (Fig. 4B). The accumulation rate of the hummock core is 100% greater than that of the hollow core. The hummock, 50 cm above the hollow, apparently is more effective at capturing Pb aerosols. Total deposition to a surface such as a bog must lie between the two extremes. Total deposition to a lake surface should be somewhat lower than the values for the hollow site. Lakes nearby have maximum accumulation rates of 2 to 5 μg Pb cm^{-2} yr^{-1} (Norton and Kahl 1987), an exaggerated rate compared to inferred atmospheric wet deposition which should be < 2 μg Pb cm^{-2} yr^{-1}. Interestingly, the Pb accumulation rate does not drop to zero prior to 1850. Soil dust has always contributed to the flux of all elements to the bog surface. Additionally, there may be very minor downward migration of anthropogenic Pb.



A



B

Figure 4. (A) Concentration of Pb in multiple sediment cores from Jerry Lake, Ontario (from Dillon and Evans 1982). Concentration based on dry mass. (B) Accumulation rate of total Pb from a hollow and hummock peat core from Big Heath, Mt. Desert Island, ME (from Norton and Kahl 1987).

SOURCE IDENTIFICATION

One can relate sources of Pb pollution to those for other elements. The synchroneity of increases among Pb, Zn, and Cu in many lakes suggests a common source, at least initially (Fig. 5). However, the V profile commonly lags behind the others, principally because a large fraction of atmospheric V is derived from the burning of oil, which increased significantly after 1920.

Different sources of Pb may be inferred from sediment records at different locations and different timing of changes in accumulation rates. Very comparable histories of Pb pollution are recorded for two high elevation lakes in the Wind River Mountains, WY (Fig. 6). The increases for anthropogenic Pb are not accompanied by increases of Zn and Cu, as is typical in eastern U. S. lakes. This suggests that the initial rise for Pb in WY was from a source other than coal burning, probably mining and smelting. Harriett Lake (Fig. 6) is in the high Sierra Nevada Mountains, CA. There, in contrast, anthropogenic Pb does not increase until about 1930-1940. This history has been linked to the use of leaded gasoline in the Los Angeles basin to the west.

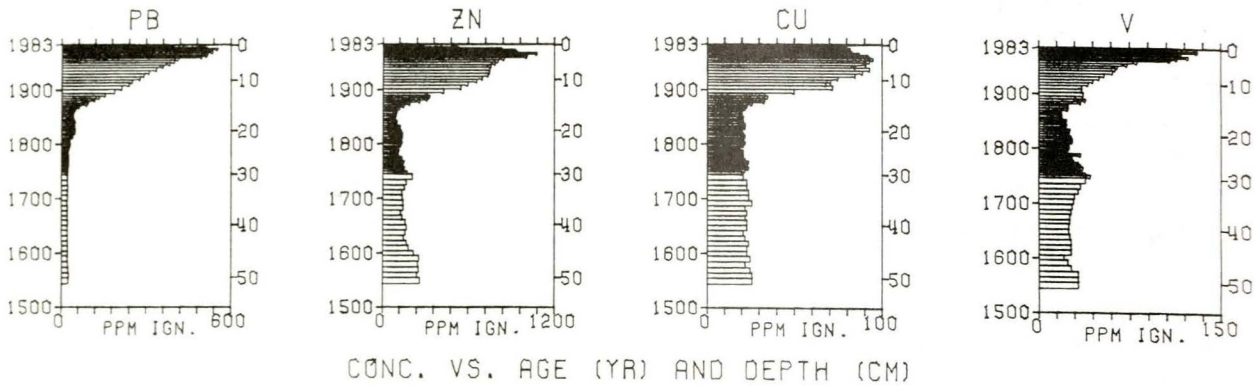


Figure 5. Concentration of four trace metals versus depth and age for a sediment core from Sargeant Mountain Pond, Mt. Desert Island, Me.

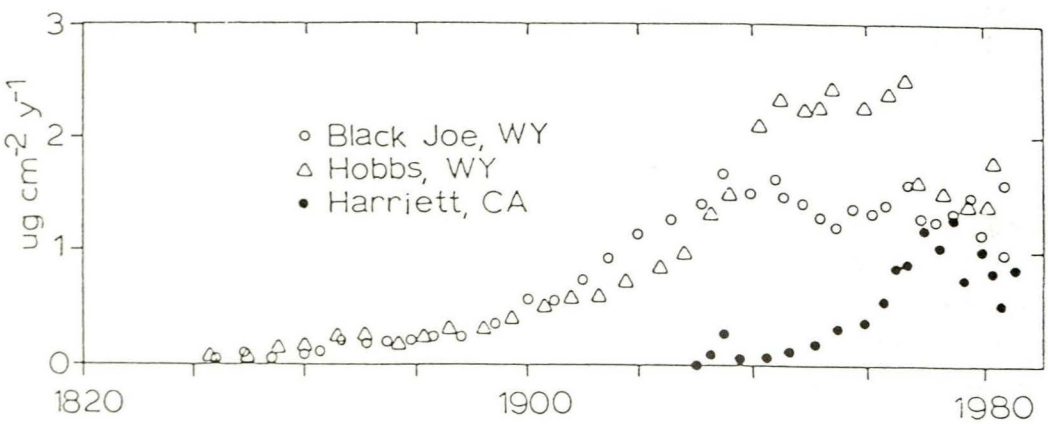


Figure 6. Accumulation rates of anthropogenic Pb for sediment cores from three western lakes (from Norton et al. 1990).

PROBLEMS IN INTERPRETATION

The examples given above illustrate possible interpretations of the Pb chemistry in dated sediment cores. Extending this approach to other elements requires considerable care. Putting aside considerations of errors in sediment dating, problems in coring and chemical analysis, and peculiarities related to the processes of sedimentation, including bioturbation, there remain several processes that affect the sediment record in an un-quantifiable way.

Chemical diagenesis of sediment may cause the: (1) relocation of trace elements within the sediment (Engstrom and Wright 1984), (2) deposition of metals in sediment not of the same age as the process of deposition (Carignan and Tessier 1985), or (3) loss of trace metals from the sediment due to changing chemistry of the water column (Kahl and Norton 1983). Additionally, many elements are only partially retained within the catchment. For example, accumulation rates for Pb and Zn in the sediments of Sergeant Mountain Pond are similar (Fig. 5). Yet, the concentration of Zn in precipitation in the same region is 4 to 5 times that of Pb (Kahl and Norton 1983). Additionally, metals accumulated in catchments may leach to the lake through time. Well documented examples of this include the steady release of ^{137}Cs from catchments, uptake by lake phytoplankton, and subsequent sedimentation (Davis et al. 1984). The slow release of Hg from catchments which previously had received substantial loading from the atmosphere (Verta 1990) is another example. As watershed soils acidify, mobilization of most trace metals is enhanced causing accelerated fluxes to or through the lake basin. The degree of retention of these metals in lake sediment may vary also as the chemistry of the water column changes, particularly the pH and dissolved organic carbon (White and Driscoll 1985).

For these reasons, the correspondence between measured air quality, atmospheric deposition, and sediment accumulation is understood only in the broadest way. The ideal lake for studying atmospheric deposition of trace metals should: (1) have no surface inlets or outlets and be a perched lake (thus having no terrestrial inputs), (2) have an oxygenated water column (to prevent mobilization of metals from the sediment), (3) be circum-neutral (to minimize mobilization of metals from the sediment), and (4) be oligotrophic (unproductive, to minimize bioturbation of sediment. Lakes of this type are relatively rare and are not commonly studied for purposes of deciphering the history of atmospheric pollution.

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THE USE OF ORGANIC FOREST SOILS AS INDICATORS OF ATMOSPHERIC DEPOSITION OF TRACE METALS

Andrew J. Friedland[1]

ABSTRACT.--The forest floor (the organic soil horizon that overlies the mineral soil) is capable of retaining trace metals that are deposited on it from the atmosphere. Different metals are retained to various degrees and metal interactions with plants vary. Under certain conditions, the forest floor can be used to estimate trace metal deposition to the surface of the forest. A portion of this paper summarizes the results of four previously published studies which, when combined, demonstrate the utility of the forest floor as an indicator of trace metal deposition, if two conditions are met: (1) all of the metal deposited on the forest floor must be retained by the forest floor; (2) uptake and cycling by vegetation must not occur. These two conditions are met to varying degrees by different elements. Because lead (Pb) is strongly retained by the forest floor and is not taken up by vegetation, estimating atmospheric deposition from accumulation in the forest floor appears to be most effective for Pb. However, recent reports from studies in the late 1980's and early 1990's suggest that perhaps even Pb is no longer as immobile as previously thought.

INTRODUCTION

The release of trace metals into the atmosphere has increased considerably during this and the previous century. In recent years, much attention has been given to the effects of increased atmospheric deposition of pollutants on major, minor and trace element cycling in terrestrial ecosystems (e.g. Adriano 1986). Studies on precipitation chemistry (Heinrichs and Mayer 1977; Smith and Siccama 1981), fog chemistry (Waldman et al. 1982), interception of cloud moisture by vegetation (Lovett et al. 1982) and dry deposition impact on vegetation (Lindberg et al. 1982) have demonstrated mechanisms for fairly high levels of metal influx to forested ecosystems.
It is known that levels of trace metals, particularly lead, in the terrestrial environment today are much higher than they were centuries ago (Shirahata et al. 1980). In the 1980's, natural sources of lead accounted for 4% of the total global Pb emissions (Nriagu 1989). Isotopic studies in the United States suggest that anthropogenic Pb may account for 64% to greater than 95% of total Pb deposition (Flegal et al. 1989). A sharp increase in atmospheric concentrations of Pb, and subsequent deposition in all environments, occurred in the 1940's as a result of increased Pb emissions from automobile exhaust. More recently, there is evidence that Pb emissions are

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decreasing, at least in some areas of the world (Trefry et al. 1985; Boutron et al. 1991), in part as a result of increased use of unleaded gasoline.

In a specific region, it is often not known what the historical patterns of trace metal deposition have been. The forest floor (the organic horizon of soil comprised of decomposing needles, leaves, twigs, that overlies the mineral soil) is an effective accumulator of metals (Schnitzer 1978) In any soil where there is an abundance of organic matter--either in an organic horizon or within the mineral soil--there will be organic matter-heavy metal interactions (as reviewed by Friedland 1990). Most of the organic matter in soils is comprised of humic substances (Schnitzer 1978). The interaction between heavy metals and humic substances has been characterized as chelation, complexation and adsorption, as well as many other terms, all of which suggest that heavy metals have a very strong affinity for organic matter in general and humic acids in particular. Although a variety of results have been obtained, a generalized listing of metal-humic substance stability constants follows (Schnitzer 1978):

$$\mathbf{Pb^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+}}$$

Incorporation of trace metals in vegetation varies by element. Lead is not incorporated in vegetation to any large degree (Smith and Siccama 1981) while other trace metals are plant-essential micro-nutrients and readily cycle in vegetation (Friedland 1990). Certain species are known accumulators of particular metals (e.g. birch accumulates zinc, cf. Gosz et al.1973).

Estimates of heavy metal retention times in the forest floor vary considerably. Lead has one of the longer retention times of any heavy metal and even here the variability in estimates is large. Based on studies that were conducted in the 1970's and early 1980's, it appeared that forest soils in North America and Europe accumulated Pb at a rate of 50 - 700 g ha^{-1} yr^{-1} (approximately 0.4 - 3.3% of the forest floor pool per year), and the mean residence times were between 150 and 500 years (Friedland et al. 1984; Friedland and Johnson 1985; Heinrichs and Mayer 1977,1980; Tyler, 1981).

Changes in the amount of trace metals in the forest floor over time are a potentially good indicator of past trace metal deposition. When only one sample at one point in time is available, the levels of metals in that sample may be a useful indicator of deposition history of the site, depending on the element studied and the background levels of that metal in soil and bedrock. The purpose of this paper is to summarize results from previous studies that demonstrate the utility and limitations of using the forest floor as in indicator of trace metal deposition.

METHODS

Forest floor (the organic horizon overlying the mineral soil) was collected in four different studies between 1980 and 1986. In each of these studies, there was an independent measure of trace metal deposition that would allow for a comparison with the accumulation estimated or measured in the forest floor. Details of the studies are shown in Table 1.

Table 1.--Sampling details for four different studies of trace metal accumulation in the forest floor.

Site	Elements Measured	Independent Method of Estimation
Camels Hump, Vermont, USA [1]	Pb, Cu, Zn	1. Samples collected in 1960's and 1980's 2. Chemical mass balance study
Northeast USA [2]	Pb	1. Regional estimates of metal deposition
Northeast USA [3]	Cu, Zn, Ni, Cd	1. Regional estimates of metal deposition
Kecskemét, Hungary [4]	Pb, Cd	1. Known age of forest and forest floor 2. Measured precipitation and dry deposition

[1] Friedland et al. 1984, and Friedland and Johnson 1985, [2] Johnson et al. 1982, [3] Friedland et al 1986, [4] Mészáros et al. 1987.

For all of the studies reported here, forest floor samples were collected using the same methods. A 15 X 15 cm template was placed on the forest floor and the surrounding material was removed to expose a block of forest floor. The sample was collected, taken to the laboratory, and oven dried at 105° C to constant weight. After grinding in a mill, samples were ashed at 475° C for 8 hours. Weight loss-on-ignition was determined and used as an estimate of forest floor organic matter content. The ash was digested with 10 ml of 6 M HNO_3 and heated to boiling on a hot plate for 20 to 30 minutes. The extract was filtered and diluted to 50 mL with deionized-distilled water. Analysis was done by flame or graphite furnace atomic absorption spectrophotometry. Further information and quality control measures are given in Friedland and Johnson (1985).

For the purpose of calculating estimated deposition rates, it is assumed that all the Pb that is deposited on the forest floor is retained in the forest floor. In fact, probably only 94-98% of the Pb in a northern hardwood temperate forest is retained (Smith and Siccama 1981). For other metals, the same assumption has been made but it doesn't appear that other metals are as strongly retained in the forest floor (e.g. Siccama et al. 1980). Furthermore, other metals such as Cu and Zn are plant-essential trace elements and thus accumulation and cycling by vegetation may obscure atmospheric deposition patterns (Friedland et al. 1986). It is also assumed that the mass of the forest floor does not decrease during the time period under study. These assumptions will be reexamined later in this paper.

RESULTS

REGIONAL STUDIES

The regional studies in the northeastern United States were one-point-in-time sampling studies. In Johnson et al. (1982), Pb amounts showed distinct patterns related to the proximity of urban areas and a smelter, the age of the forest floor and elevation of the study sites. Greatest amounts of Pb were present near the "Northeast Corridor," an area of heavy motor vehicle traffic and in the area surrounding a zinc smelter. In these same areas, Friedland et al. (1986) found that Cu, Zn, Ni and Cd did not show obvious patterns related to the same factors. There are at least two reasons for these differences: (1) sources of Pb and the other metals are different, and (2) the concentration of Pb in the forest floor (80 to 225 mg kg^{-1}) is much greater than in the underlying mineral soil (10 to 22 mg kg^{-1}); concentrations of Cu, Zn, Ni and Cd in the forest floor and mineral soil are fairly similar (Friedland et al. 1986; Friedland 1990).

TEMPORAL CHANGE STUDY

The Pb content of the forest floor was determined along an elevation gradient on a mountain in Vermont, USA in 1980 and 1981 (Friedland et al. 1984) and in 1965 (Siccama 1974). Based on the change in Pb concentration, and an estimate of change in forest floor mass between 1965 and 1980, Pb accumulation was calculated. This accumulation was estimated to be an approximation of atmospheric Pb deposition (Table 2). In a subsequent study (Friedland and Johnson 1985), a chemical mass balance study was made at one elevation on the same mountain and a similar estimate of Pb deposition to the forest floor was made (Table 2). The results in Table 2 show fairly good agreement between independent methods for estimating Pb accumulation.

Table 2.--Rates of Pb accumulation in the forest floor along an elevation gradient in Vermont, USA, as determined by changes in forest floor chemistry and by independent methods.

Elevation (m)	Deposition Estimate From Change in Forest Floor[1] (g ha^{-1} yr^{-1})	Other Deposition Estimates (g ha^{-1} yr^{-1}) and Method Used	
550	175	300	Accumulation in mosses [2]
880	600		None available
1000	520	660	Chemical mass Balance [3]

[1] Friedland et al. 1984, [2] Groet 1976, [3] Friedland and Johnson 1985

PRECIPITATION AND SOIL SAMPLING STUDY

Lead and cadmium (Cd) deposition were monitored in precipitation and dry deposition from 1981 through 1986 (Mészáros et al. 1987, 1988), and Pb and Cd deposition rates were estimated at 99 and 7.2 g ha^{-1} yr^{-1}, respectively. In 1986, forest floor was collected from a pine forest adjacent to the deposition monitoring site. Because the age of the pine forest, and the age of the forest floor in the pine forest, were known to be approximately 18 years old, Pb and Cd accumulation during that time could be determined from total Pb content of the forest floor. Average Pb and Cd accumulation rates were estimated at 50 and 1.3 g ha^{-1} yr^{-1}, respectively (Mészáros et al. 1987). Differences between the two estimates for each element could represent imprecision in either method but it was considered encouraging that the Pb estimate differs by less than a factor of two.

EVALUATION OF TRACE METAL MOBILITY ASSUMPTIONS

In 1988, Herrick and Friedland (1990) measured Pb concentrations in forest floor on 19 mountains in the northeastern United States and noted that Pb concentrations were somewhat lower than had been reported previously. In 1990, Craig (1991) resurveyed forest floor sampling sites originally sampled in 1980 (Johnson et al. 1982) and found significant decreases in Pb concentration (17% decrease) and amount (12% decrease) (Craig 1991, Friedland et al. 1991). Because of the reduced Pb emissions in the northeastern United States mentioned earlier (Trefry et al. 1985; Boutron et al. 1991), it was expected that the annual accumulation rate of Pb determined in 1990 would be much lower than it had been in 1980. However, because of the large mean residence times of Pb in forest floor (150-500 yrs), also mentioned earlier, it was not expected that Pb concentrations or amounts would decrease measurably over 10 years. The measured decreases were much greater than expected.

The process by which Pb concentrations and Pb amounts decreased is not immediately evident. Since the average forest floor mass at the study sites did not change significantly in the 10-year period (Craig 1991; Friedland et al. 1991), there was no dilution of the Pb concentration by increased amounts of organic matter (c.f. Siccama et al. 1980). It is more likely that Pb has migrated from the forest floor into the underlying soil horizons. The movement of Pb to horizons below the forest floor has been observed previously (Turner et al. 1985; Friedland and Johnson 1985; Driscoll et al. 1988). However, none of these authors believed that the measured quantities of Pb movement would lead to appreciable Pb leaching over a relatively short period of time (i.e. 10 years). Apparently, either the measured Pb concentrations in these studies were an underestimate, or the water fluxes used to estimate total Pb export were an underestimate, or Pb exits the forest floor in some other manner than via soil solution. Regardless of the mechanism, it appears that the forest floor may not record the history of atmospheric Pb deposition as well as previously thought. It has been proposed that peatlands in the northeastern United States, which had also been thought to preserve the atmospheric Pb deposition record, have been leaching Pb more readily than had previously been believed (Urban et al. 1990). Both of these studies took place in the late 1980's, when Pb deposition was much lower than during the

previous 30-40 year period. It is not clear if the changes in Pb deposition rates were, in part, responsible for the apparent change in the behavior of Pb, or if some other regional or global factor is responsible.

CONCLUSIONS

There are many instances when it is desirable to obtain a "pollution index" of metal deposition rates for periods of time in the past when environmental monitoring was not conducted. The forest floor is a material that has the potential to be a cumulative collector of trace metals. Different metals behave differently in soils and with vegetation. In addition, the soil levels of certain metals from anthropogenic inputs are not substantially different from the levels found naturally in the environment. However, some metals, such as Pb, are present today at much higher levels than in the past, mostly because of atmospheric deposition from anthropogenic activities. The atmospheric "signal" for Pb stands out clearly above the background levels found in most soils. Thus Pb, and in some cases other elements, can be effectively monitored from total amounts, and changes in amounts, found in the forest floor. However, recent evidence suggests that lead may no longer be as immobile as previously thought. This new finding may reduce the effectiveness of lead as a tracer of past environmental pollution.

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TRACE METAL IMPACT ON PLANTS: MEDIATION BY SOIL AND MYCORRHIZAE

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ABSTRACT.--In this paper, we review important aspects of the soil cycle of trace metals with respect to assessing toxic impacts of atmospheric deposition on vegetation. In general, soil chemical processes immobilize trace metals in surface soils, and render only a fraction of total input available to plants. Mycorrhizal fungi may reduce the uptake of available metals by plants. However, toxicity of metals to fungi may limit this benefit as well as others, such as nutrient acquisition, leading to reduced plant growth. Good predictive models of the degree of impact which trace metal deposition will have on vegetation must account for buffering capacity of different soils and metal tolerance of different mycorrhizal fungi.

INTRODUCTION

Trace metal contamination is being widely detected in soils of developing and industrialized countries (Jones 1990). The source appears to be broad atmospheric dissemination of metal-containing dusts, primarily from mineral smelting and refining activities, burning of fossil fuels, and from incineration of municipal wastes. In industrialized regions, anthropogenic input of metals to soils is occurring at rates far greater than natural inputs (Puxbaum 1990). Due to very low natural removal rates, there is growing concern that soils in some developed countries have become or will soon become overloaded with trace metals (Nriagu and Pacyna 1988).

Trace metals refer to elements that occur naturally in soils in very small amounts. In these very small quantities, some trace metals, such as Co, Cu, Zn, Mn and Mo, are nutrients to plants. In greater amounts virtually all metals are toxic to plants. Non-nutrient elements of current importance as environmental pollutants include As, Cr, Ni, Cd, Hg, and Pb. Acute toxicity problems which normally occur in highly contaminated soil near point sources are loss of vegetation, soil sterility, and eventual soil erosion. Widespread low-level accumulation of trace metals in soils, however, causes subtle, and potentially more far reaching, problems through 1) uptake by plants and movement in the food chain, 2) disappearance of metal-intolerant species, and 3) overall reduction in plant growth. Since micronutrient deficiencies are uncommon in natural ecosystems, any addition of metals to soils has potential for adverse impacts on plants.

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In order to predict the impact of trace metal deposition on vegetation, we must know not only how large the input is, but also how sensitive vegetation is to that input. To a great degree, toxic impact on vegetation is controlled by below-ground processes determining the amount of metals chemically available for uptake by plants. A simple model of these processes is illustrated in Figure 1. Trace metals from wastes may be taken up by plants, leached out of the soil, or transformed into unavailable forms. Recent research suggests that plant uptake of trace metals from the soil available pool is also significantly modified by fungal activities of mycorrhizal roots.

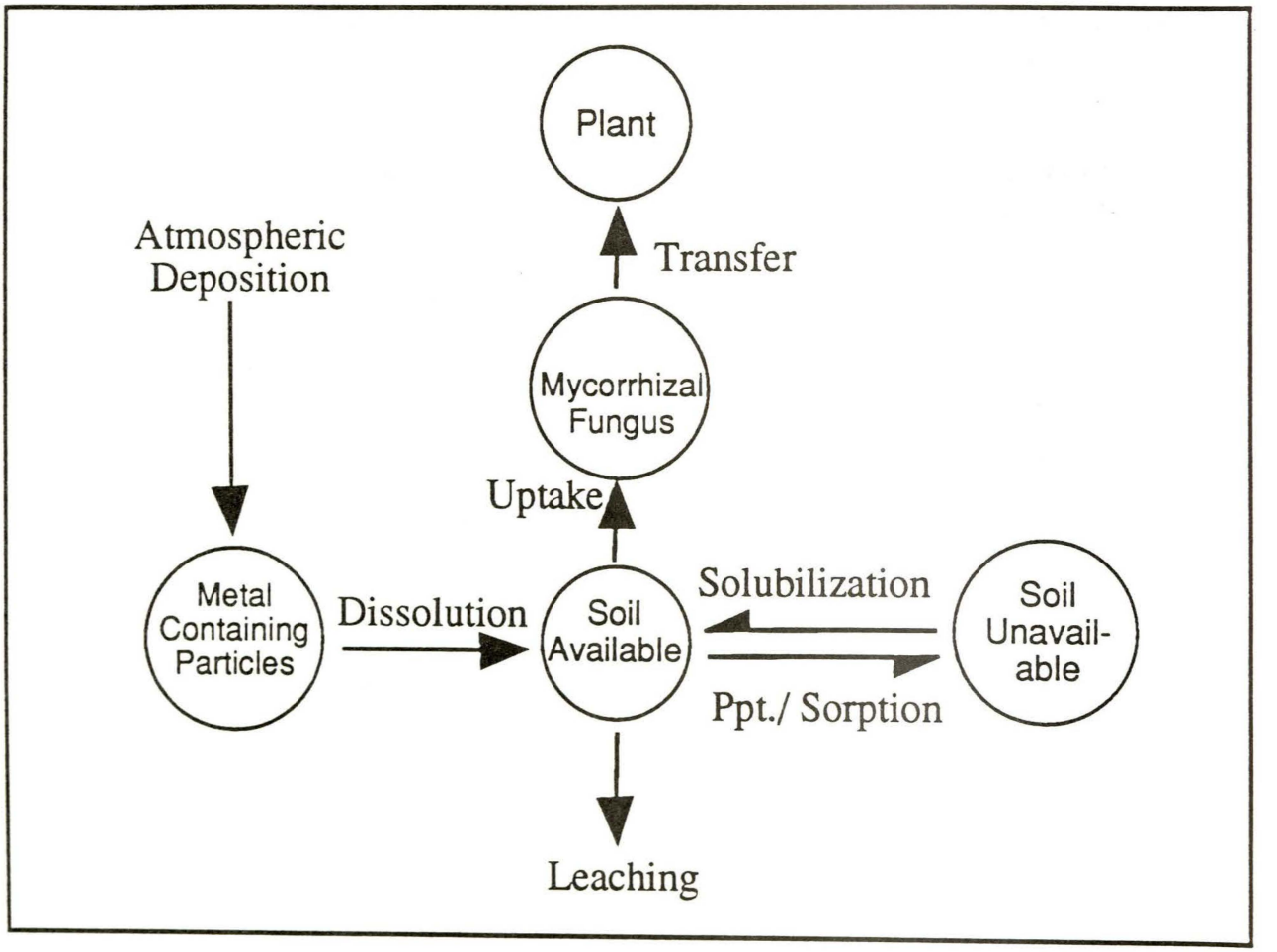

Figure 1.--Important below-ground processes which determine the impact of trace metal deposition on plants (Adapted and modified from Adriano 1986).

The levels of trace metal input which result in toxic impact on plants are highly variable. Table 1 shows total soil concentrations of various metals in natural soils and levels at which some metal toxicity of plants may occur. The range of critical toxic levels reported here represents a range of sensitivity among agricultural plants to metals in agricultural soils. If non-agricultural soils and plants were included, critical toxic levels would likely range much more widely. This variability is too large to allow useful predictions of resource impacts based on total deposition. We can improve our predictions by considering the sources of variation. Some variability can be attributed to metal tolerance differences between plant species (Baker and Walker 1989; Logan and Chaney 1983). However, considerable variation can also be traced to differences in soil properties and, perhaps, mycorrhiza types. Variable properties of different soils and mycorrhizae affect the partitioning and availability of metals and, subsequently, plant uptake. As a result, plant communities which occur on certain soil types and which associate with certain mycorrhiza types have greater sensitivity to atmospheric deposition of trace metals than others.

Table 1.--Concentration of selected trace metals in soils (Adapted from Alloway 1990).

Element	Natural soils range[1] (mg kg^{-1})	Critical toxic range[2] (mg kg^{-1})
Hg	0.01 - 0.5	0.3 - 5
Cd	0.01 - 2	3 - 8
Mo	0.1 - 40	2 - 10
As	0.1 - 40	20 - 50
Co	0.5 - 65	25 - 50
Cu	2 - 250	60 - 125
Pb	2 - 300	100 - 400
Ni	2 - 750	100
Cr	5 - 1500	75 - 100
Zn	1 - 900	70 - 400

[1] Source: Bowen 1979.
[2] Soil concentrations above which plant toxicity is possible.
[3] Source Kabata-Pendias and Pendias 1984.

SOIL AVAILABILITY

Trace metals are usually deposited on soils in the form of dust particles, often contained in water droplets, and carried great distances from sources. (A notable exception is Hg vapor emissions from coal combustion and municipal incinerators (Freedman and Hutchinson 1981)). These fine dust particles, formed at high temperature, are unstable under soil conditions and gradually dissolve. Once dissolved, metal ions are available for uptake by plants, leaching, and for precipitation/complexation reactions with natural components of the soil (Fig.1). These precipitated and complexed metals are unavailable for uptake by plants, but may re-enter the available pool by solubilization. The size of this available pool is controlled by transformations between available and unavailable forms of metals.

The soil available pool of metals is that portion of the total quantity in the soil which plants can absorb. It consists of 1) dissolved metals ions in the bulk soil solution, and 2) dissolved metal ions electrostatically immobilized by attraction to charged soil colloids, collectively called the ion exchange complex. The unavailable pool consists mainly of precipitates of carbonates, phosphates, sulfides, and silicates, and complexes with organic matter and hydrous oxides of Fe, Al, and Mn in soils. Normally, soils have large ion exchange complexes and abundant reactive components providing them with a large capacity to immobilize trace metals.

Partitioning of metals between available and unavailable pools is controlled by thermodynamics and kinetics of the various reactions in which they are involved. Adsorption of dissolved metal ions to the ion exchange complex occurs instantaneously and strongly, often displacing less tightly held nutrient ions such as K and Ca. Precipitation and complexation of ions from the soil solution and the exchange complex into solid forms can occur rapidly as well. Thermodynamics favor precipitation and complexation reactions to the degree that only a small fraction of total input remains in ionic forms. Highly effective metal immobilization processes in soil result in negligible leaching of metals. As a result, virtually all trace metals which are deposited on soil are retained, often within a few centimeters of the surface unless the soil is disturbed, as by tillage or erosion.

Although soil capacity for reacting with metals is large, there are narrower limits to the capacity of various reactive components. Initial inputs can be expected to precipitate and complex into the most insoluble forms, with subsequent inputs immobilized in forms of higher solubility. In this way, continued metal input leads to greater plant availability. At low rates of input, accumulations may occur over many years before toxic levels are reached.

The proportion of the trace metals in soil which are available to plants is variable and depends upon soil conditions. Important properties of soils which determine their capacity to immobilize and sequester metals include 1) soil pH, 2) redox potential, and 3) amount and type of clays and organic matter (Adriano 1986). Of these, soil pH is the parameter most consistently identified as controlling metal availability. In general, availability of trace metals in soil increases with decreasing pH. With the exception of Mo, trace metals are more soluble under acid conditions due to hydrolysis of hydrous oxides and solubility of phases such as carbonates and phosphates. Low pH also lowers metal ion adsorption to pH-dependent exchange sites on clays and organic

matter due to H^+ ion competition. Redox potential can be very important in wet soils. Low redox potential, such as brought about by flooding, reduces availability of metals as lower oxidation states of most trace metals are less soluble. Under reducing soil conditions, sulfides of Cd, Zn, Ni, Co, Cr, and Pb can form which are highly insoluble, thereby greatly reducing plant availability of these metals compared to well-oxidized soils. Some exceptions include Mn and Mo where availability may increase under reducing conditions. Clays and organic matter are particularly effective at immobilizing and sequestering trace metals. Soils high in clay and organic matter content have an abundance of both readily reactive components and surface area for reactions to take place. The ion exchange complex of soils is composed primarily of highly decomposed organic matter and crystalline silicate clays. In addition, many cationic trace metals (e.g. Cd, Co, Cu, Ni, Pb, Zn) exhibit high affinity for binding to organic matter to form complexes. Metals contained in these organic complexes are unavailable to plants. Certain types of clays, those composed of Fe, Al, and Mn hydrous oxides, promote complexation of metals into amorphous matrices of these oxides. These oxides may be especially important for complexing oxyanions of As, Cr, and Mo (Korte, et al. 1976) and along with organic matter, provide the principle control on fixation of trace metals in soils (Jenne 1977).

From a long-term standpoint, virtually all metals accumulated in soils are potentially available to plants. This is because soil conditions can change to favor solubilization of unavailable forms back into the soil available pool. Soil acidification and drainage are examples of some changes which can increase the availability of metals to plants. Fortunately, solubilization reactions may be slow, and over time, metals are rendered less readily solubilized as smaller, more reactive crystals and amorphous complexes combine into larger, less-reactive particles.

The capacity of soils to immobilize and sequester trace metal inputs is geographically variable. Soil factors such as pH, soil texture, organic matter content can differ greatly from one region to another as well as from one topographic position on the landscape to another. Most surface soils in the U. S. range in pH from about 4.0 to 8.0, with clay contents of 2 to 40%, and 0.5 to 10% organic matter. This wide range of variability in soil properties suggests a great deal of variability in the availability of metals deposited in different soils. As an example, fine-textured, high pH soils would be capable of sequestering a larger quantity of metals in the unavailable pool, and thus have less potential for impact on vegetation, than coarse-textured, acid soils. This example illustrates a possible improvement in predictability of trace metal impacts of vegetation by accounting for geographical differences in a few important soil properties.

MYCORRHIZAL ACTIVITY

There is increasing evidence that mycorrhizal fungi play an important role in the impact of trace metals on vegetation. Mycorrhizae are the primary absorbing organs of most plants (see review by Harley and Smith 1983), so it is reasonable to expect that they have some influence on trace metal uptake. But the role of mycorrhizae in plant response to metals in soils may be more complex than just modifying plant uptake. Metals may also detrimentally affect other mycorrhizal processes which are beneficial to plants.

Mycorrhizae are a symbiotic association between certain soil fungi and plant roots. Fungal hyphae colonize young roots by growing within root tissues, and from there out into the soil (Fig.2). The mycorrhizal fungus obtains food from the host and, in return, absorbs nutrient ions from soil and releases them to root cells. Mycorrhizal fungi also protect plant roots from pathogens (Gianinazzi-Pearson and Gianinazzi 1983), enhance plant drought tolerance (Dosskey, et al. 1991), stimulate photosynthesis (Dosskey, et al. 1990), and modify root growth (Slankis 1973). Mycorrhizal symbiosis in nature is highly evolved and is the norm, not the exception, of root condition (Trappe 1977).

The importance of mycorrhizae to plant health should not be underestimated. It is estimated that 95% the worlds' plant species belong to families that form mycorrhizae (Trappe 1977). Although most of these plant species can be grown alone in fertilized culture, in nature, normal growth and, in some cases survival, of virtually all of these plants is impossible without mycorrhizal fungi. How metals affect mycorrhizae and how mycorrhizae influence plant uptake and toxicity could be very important factors for predicting sensitivity of vegetation to trace metal deposition.

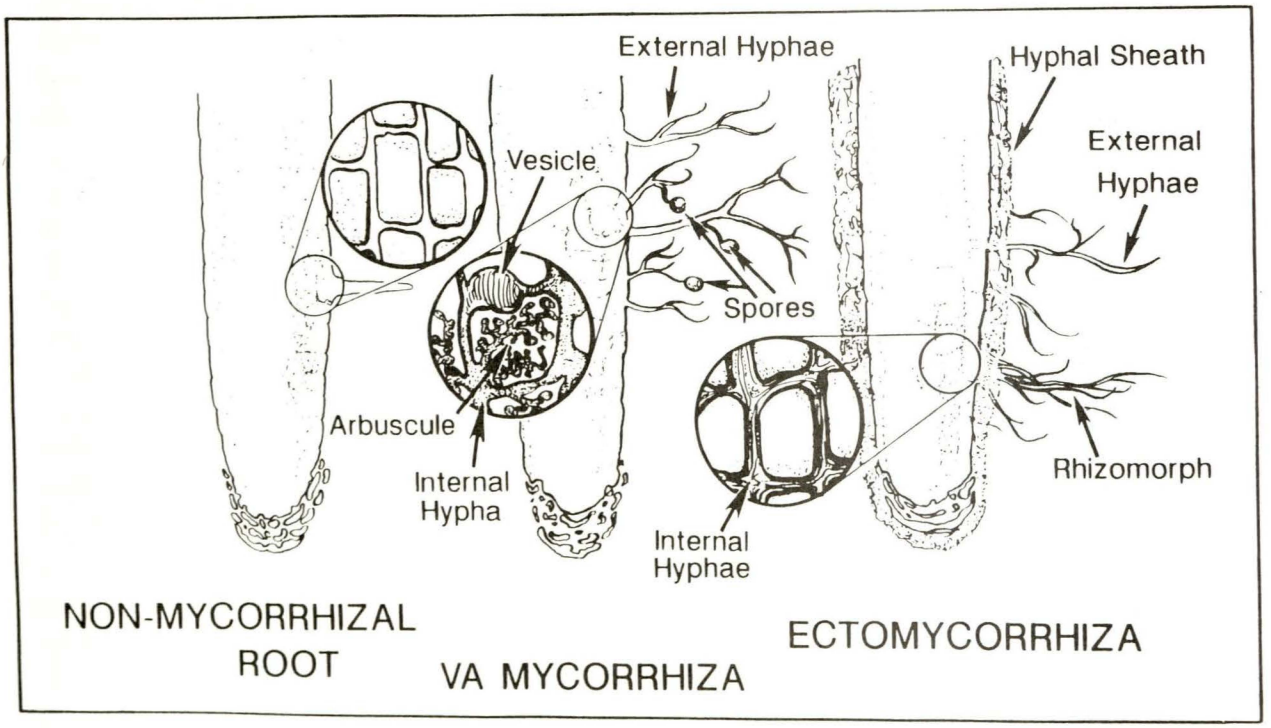

Figure 2.--Structure of two common types of mycorrhizae compared to an uncolonized root.

Under natural soil conditions, mycorrhizae are particularly important to plant growth because they absorb nutrients which are in short supply. Facilitated uptake of P, a fairly immobile element in soil required by plants in very large quantities, is an often-cited example of this importance. Mycorrhizae are also important suppliers of immobile and unabundant micronutrient metals. The facilitation mechanism appears to be dominantly one of more complete exploration of soil by a profusion of fine fungal hyphae than is possible by roots. The benefit of nutrient acquisition is clearly the dominant factor contributing to improved growth of colonized plants (Ruehle and Marx 1979).

Under conditions where trace metals were added to soil, a few studies showed that presence of mycorrhizae can exacerbate adverse impacts on plants (Jones and Hutchinson 1986; Killham and Firestone 1983). This might be due, in part, to the fungus facilitating metal uptake to levels which reduce plant growth (Killham and Firestone 1983) or to metals inhibiting beneficial mycorrhizal processes. Metals have been shown to be toxic to mycorrhizal fungi (Colpaert and van Assche 1987; McCreight and Schroeder 1982) and suppress colonization (Dixon and Buschena 1988; Gildon and Tinker 1981, 1983). Reduced mycorrhizal activity by fungal toxicity or suppressed colonization level could lead to nutrient deficiencies (Lambert, et al. 1979; Timmer and Leydon 1980) and other problems such as root disease and drought stress. In this way, the toxic effect of metals on plants can be indirect, by acting on beneficial mycorrhizal fungi.

Many studies confirm that some mycorrhizal fungi have a large capacity for protecting host plants from excessive metal uptake (Wilkins 1991). The fungi take up metals from soil, but do not transfer them to the plant (Bradley, et al. 1982). Instead, the metals are sequestered in the fungus (Wasserman, et al. 1987). Apparently, so long as these fungi can tolerate high metal concentrations in their tissues, they appear able to buffer impacts of high levels of metals in soil on vegetation (Dixon and Buschena 1988).

Facilitated metal uptake and metal exclusion activities of mycorrhizal fungi may be reconcilable results. A recent study indicated that mycorrhizae enhance metal uptake by plants at low soil metal levels, but protect plants from excess uptake at high soil metal levels (Heggo, et al. 1990). Therefore, both mechanisms are possible depending on soil metal level. Mycorrhizal capacity for metal uptake and exclusion from plants (Jones, et al. 1986) and tolerance to metals (McCreight and Schroeder 1982) vary greatly between species of mycorrhizal fungi and even between isolates of the same species (Gildon and Tinker 1981). If the colonizing fungus is tolerant of metal contamination, plants may experience limited toxic uptake or protection by exclusion depending on soil metal level. If the fungus is metal-intolerant, plants may show "toxic" effects due to nutrient deficiency, root disease, or other problems related to reduced colonization or activity. Either way, it is clear that host plant response to metals in soil is closely related to fungal tolerance.

Impacts of metals on plants caused by toxicity of fungi may be difficult to detect based on the level of mycorrhizal colonization. Many species of fungi can exist in symbiosis on a single root system (Marks and Foster 1967; Molina, et al. 1978), and each species probably contributes to various plant benefits of symbiosis in a slightly different way, just as metal tolerance and exclusion activities differ among mycorrhizal fungi. Added soil metals may lead to disappearance

of intolerant fungal species and proliferation of more tolerant fungal species. However, metal tolerant fungi may not be the fungal symbionts which are most effective at nutrient uptake or pathogen protection or other benefits. As a result, plants may actually get improved metal protection over time, but at the cost of reduced nutrition and pathogen protection. In effect, plants would exhibit reduced growth even before toxicity of mycorrhizal fungi is revealed through reduced colonization levels.

There may be a pattern of fungal variability which can be exploited for identifying and predicting trace metal impacts on vegetation. Some general types of mycorrhizal fungi, which associate with specific taxa of plants, may mediate between soil available metals and plants in different ways than other types. It has been suggested that metal exclusion activity is generally stronger for mycorrhizal types which develop a large fungal mass than those which do not (Bradley, et al. 1981). Conifers and a few deciduous trees form ectomycorrhizae with fungi which typically develop thick sheaths of fungal hyphae over root surfaces and a great deal of external hyphae in the soil (Fig.2). Most crop and herbaceous plants, and many deciduous trees and shrubs, form vesicular-arbuscular (VA) mycorrhizae with a taxonomically different group of fungi, which typically develop much less abundant fungal growth. If Bradley's hypothesis is correct, then VA mycorrhizae-forming herbaceous plants and deciduous trees, in general, would be more sensitive to metal contamination of soil than conifers and their more metal-tolerant fungal symbionts.

SUMMARY

We've reviewed a general conceptual model where vegetation impacts of metals depend on total input, soil availability, mycorrhizal tolerance and plant tolerance of metals. Soil and mycorrhizal processes buffer impacts of soil metals on plants. Adverse impacts on vegetation occur when soil and mycorrhizal buffer systems become overloaded.

Soils typically have a large capacity to buffer metal inputs by transforming them into forms unavailable to plants. Metal additions accumulate in surface soils and have adverse impacts when toxic available levels are eventually reached, or when soil conditions change to release unavailable metals to available forms. Coarse-textured soils with minimal organic matter and low pH typically have the lowest ability to sequester metal inputs in unavailable forms.

Mycorrhizae appear to be able to buffer root uptake of available metals from soil by sequestering the metals in fungal tissue. However, toxicity of metals to fungi could eventually lead to reduced plant growth from nutrient deficiency or other problems. There is a great deal of variability in metal tolerance among mycorrhizal fungi and the ecological consequences of this variability with respect to soil contamination has yet to be researched. A theory has been proposed which implies that plants which form ectomycorrhizae may be capable of sustaining greater metal inputs before experiencing adverse impacts than those forming VA mycorrhizae. If this theory is correct, metal contamination could cause subtle conversions in plant community species composition long before metal toxicity problems in plants become evident. In mixed forests, for example, metal contamination may lead to disappearance of metal-intolerant, VA mycorrhizae-forming plant species in favor of ectomycorrhizal plants including conifers.

Based on soil types and, perhaps, mycorrhizal types, we can expect significant geographical differences in impact of metals on vegetation. Taking these variables into account should allow better assessment of the potential for vegetational impacts from atmospheric trace metal deposition.

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ATMOSPHERIC DEPOSITION: EVIDENCE IN FOREST ECOSYSTEMS

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ABSTRACT.-- Although precipitation monitoring has identified trends in atmospheric deposition of pollutants, clear evidence for that deposition in terrestrial systems has been scarce. Correlations among ecosystem properties, and natural levels of elements that are also pollutants, obscure detection of pollutants in terrestrial systems. We collected samples of tree wood, surface litter (forest floor), and mineral soil from forest stands across the forested portions of Minnesota, Wisconsin, and Michigan. The stands were located along a well-documented gradient of wet sulfate deposition. We used analysis of covariance, elemental ratios, and subtraction of background levels in our analyses. Sulfur in forest floor, in surface mineral soil, and in tree wood followed the gradient in deposition, with increasing levels from west to east. Similar trends were also found for other atmospheric pollutants such as Pb, Cd, and Hg in the forest floor and mineral soil components. Soil-derived elements, such as K and P, had opposite trends, decreasing from west to east. Atmospheric deposition is differentially affecting forest ecosystems in the northern Lake States.

INTRODUCTION

The National Atmospheric Deposition Program / National Trends Network (NADP/NTN) and similar monitoring efforts have identified clear geographic trends in deposition of materials from the atmosphere. Most attention has been focused on atmospheric pollutants that are derived from industrial activities. Although there is strong evidence for the effects of some of these pollutants in aquatic systems, evidence for effects in terrestrial systems is equivocal. Clear evidence of terrestrial effects of pollutants has primarily come from intensively-studied "hot spots" (e.g., Solling Plateau, Ulrich 1983; Netherlands, van Breeman and Jordens 1983). The covarying nature of ecosystem properties and native levels of potential pollutants obscure attempts to find patterns that unequivocally indicate that ecosystems are receiving and storing materials from the atmosphere.

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We investigated 169 forest stands that lie on a well-established gradient of wet sulfate deposition (Harris and Verry 1985, Verry and Harris 1988) from northwestern Minnesota through eastern Michigan. We sampled and analyzed both soil and tree woody tissue from those stands, and evaluated trends in sulfur (S), lead (Pb), cadmium (Cd), and mercury (Hg), all elements commonly recognized as atmospheric pollutants. This paper will review and summarize the results of those studies.

METHODS

The sampling area was divided into five geographic zones; division boundaries corresponded to the 1, 2, 4, and 8 kg $ha^{-1}yr^{-1}$ isolines of an acid sulfate deposition gradient (Nichols and McRoberts 1986, Verry and Harris 1988) (figure in David et al. 1988). Data from USDA Forest Service inventory plots from the region were screened to identify a subpopulation with a limited range of tree densities, ages, and productivities. A stratified random sample of 169 plots was selected from that subpopulation of plots to equitably distribute five forest types among the zones. The five types were: balsam fir (*Abies Balsamea* (L.) Mill.) (n=24), northern hardwoods dominated by sugar maple (*Acer saccharum* Marsh.) (n=41), jack pine (*Pinus banksiana* Lamb.) (n=39), red pine (*Pinus resinosa* Ait.) (n=27), and aspen (*Populus tremuloides* Michx.) (n=38). The plots occurred on a variety of landforms; about one-fourth were on soil mapping units dominated by Alfisols, one-fourth by Entisols, one-fourth by Spodosols, one-sixth by Inceptisols, and one-tenth by other soil orders or were on unmapped soils (Ohmann et al. 1989). Precipitation and temperature differed significantly among zones, ranging from 64 cm annual precipitation and 3.8°C mean annual temperature in zone 1 (northwesternmost) to 81 cm and 5.8°C in zone 5 (southeasternmost).

FIELD SAMPLING

Sampling was conducted on the inventory plots, comprised of 10 subplots in roughly an elliptic configuration with a total plot area of about 0.4 ha. Field measurements were made from June through October 1985. At every other subplot (n = 5), a dominant or codominant tree of the most prevalent species was used to define a location for soil sampling. Forest floor (i.e., surface organic litter) and surface mineral soil (0 to 25 cm) samples were collected at three locations around each sample tree. Forest floor was quantitatively sampled within a known area, and included all organic material down to the mineral soil surface as well as sticks and roots. Mineral soils were sampled beneath the point at which forest floor had been collected. Mineral soil bulk density was sampled at one location near each sample tree.

At one location at each of three randomly-selected sample trees, soil sampling continued to 1 meter, and samples were collected from the 26 to 50 cm, 51 to 75 cm, and 76 to 100 cm depths. These subsurface samples were composited in the field to yield one subsurface sample for each 25 cm depth from each plot. All organic and mineral soil samples were placed in Whirl-pak plastic bags, cooled immediately, and frozen upon return to the laboratory (usually within 48 hours). Multiple woody samples were collected from each sample tree by increment borer.

Increment cores, including a minimum of 30 years of annual growth rings, were kept frozen until processed.

LABORATORY ANALYSES

After thawing, the three forest floor samples associated with each sample tree were bulked and homogenized. One subsample was removed, oven-dried (75°C), and ground; another was kept moist at 4°C. After thawing, the three surface mineral soil samples associated with each tree were also bulked and sieved while moist. After sieving, mineral soils were mixed and a subsample was oven-dried (105°C) and ground; the moist remainder was retained at 4°C. This procedure yielded five forest floor and five surface mineral subplot samples from each plot. Aliquots of the moist samples were also air-dried and further composited to yield single samples of forest floor and surface mineral soil for each plot.

The oven-dried subplot samples were used for analysis of nitrogen (N), S, and loss on ignition (LOI) (David et al. 1988). Samples were analyzed for total S with a LECO SC-132 automatic analyzer, and for total N by semimicro Kjeldahl. Analysis for LOI was by ashing at 450°C (David et al. 1988). The oven-dried subplot samples of forest floor were ashed overnight, the ash was further digested in hot HCl, and acid solutions were analyzed for multiple elements including potassium (K), phosphorus (P), Pb, and Cd by inductively coupled plasma atomic emission spectrometry (ICP; ARL model 137) (Grigal and Ohmann 1989). The air-dried plot samples were digested with sequential additions of concentrated HNO_3, H_2SO_4, and HCl. After digestion, Hg was determined by cold vapor atomic absorption spectroscopy in conjunction with a gold trap (Nater and Grigal, unpublished).

Tree cores were thawed and the 1956-1985 growth was divided into three 10-year growth periods. Length of each increment was measured, and then increments were grouped with others of the same growth period from each tree (i.e., all 1956-1965 segments aggregated) and oven-dried at 65° C. Nitrogen was analyzed by semimicro Kjeldahl, with N determined colorimetrically on a Technicon Auto Analyzer System. Total S was by ICP (Ohmann and Grigal 1990).

STATISTICAL ANALYSES

One and two-way analyses of variance (ANOVA) (Snedecor and Cochran, 1967) were used to determine significance of differences in variables among forest types and zones; mean separation was usually by Bayes least significant difference (BLSD) (Smith, 1978). Linear regression analyses (Wilkinson, 1986) were also used. In some cases, to be discussed below, the ANOVA included covariates. Our interest in this study was in geographic patterns, and hence differences among forest types will not be discussed. Because forest types were sampled nearly equally among zones, differences in elemental levels due to variation in abundance of specific forest types did not significantly affect the geographic patterns. In the ANOVAs, interactions between forest type and zone were not statistically significant.

RESULTS AND DISCUSSION

ATMOSPHERIC DEPOSITION

The goal of our experimental design was establishment of geographic zones with significant differences in atmospheric deposition. Atmospheric deposition of S at each plot was estimated from the quantity of precipitation recorded at the nearest U.S. Weather Service station, and the concentration of SO_4 in that precipitation (Shifley 1988). The latter was based on an equation relating latitude and longitude to concentration using 1983 NADP/NTN data. This relationship was strong (R^2= 0.94) (Shifley 1988). Sulfate deposition from these estimates was significantly different among zones ($p < 0.01$), ranging from 156 equiv. ha^{-1} in zone 1 (westernmost) to 380 equiv. ha^{-1} in zone 5 (easternmost) (David et al. 1988). These results are consistent with the gradient based on NADP and other stations as reported by Harris and Verry (1985).

SULFUR IN SOIL - ANALYSIS OF COVARIANCE

Our interest was in soil S, but geographic trends were obscured by organic matter dynamics. Decomposition and other processes affecting organic matter generally affect N and S concentrations similarly. In our data set, total N and S concentrations were highly correlated (R^2=0.96, n = 1765, $p < 0.0001$). We therefore tested differences in S concentrations by ANOVA with N as a covariate. In both forest floor and surface mineral soil, adjusted total S concentration was relatively constant across zones 1 through 3, and increased significantly in zones 4 and 5 ($p < 0.05$) (Fig. 1) (David et al. 1988). Atmospheric deposition is a reasonable explanation for the increase of 15% in total S in zone 5.

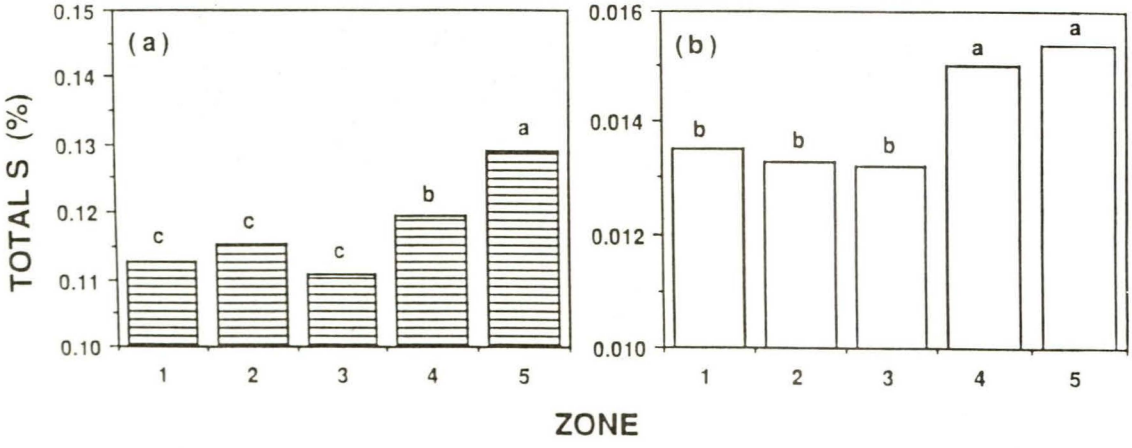

Figure 1.--Adjusted total S concentrations in forest floor (a) and surface mineral soils (b) by zones from 1 in northwestern Minnesota to 5 in southeast Michigan. Data presented are means based on two-way ANOVA, using percent N as a covariate. Means indicated by the same letter are not significantly different (from David et al. 1988).

Concentration data were converted to N and S mass on each plot. There were no trends in N mass with zone, but S mass could be predicted as a function of N mass, latitude, and longitude (R^2= 0.96, $p < 0.0001$ for forest floor; R^2= 0.87, $p < 0.0001$ for surface mineral soil). Based on this relationship, and holding N constant, the difference in mass of S from northwestern Minnesota to southeastern Michigan is 14 kg ha^{-1} in forest floor and 100 kg ha^{-1} in mineral soil (David et al. 1989). Differences in wet deposition, based on the 1983 data, were about 5 kg ha^{-1} yr^{-1}. Considering additional S additions by dry deposition, it is clear that less than 20 years of deposition would account for the differences in mass of S stored in the soil. Tree uptake and litter return and microbial immobilization are probably important processes for S retention in these systems (David et al. 1989).

SULFUR IN WOOD - ELEMENTAL RATIOS

As was the case for soils, S and N in tree woody tissue were closely related, ranging from a correlation coefficient of r = 0.31 for aspen to r = 0.81 for jack pine (Ohmann and Grigal 1990). We used molar ratios of S to N to compensate for this covariation. We also evaluated length of the 10-year increment as a covariate to compensate for elemental dilution or concentration due to variation in tree radial growth. The ANOVAs showed no significant effect of increment length as a covariate on molar ratios for any of the three growth periods. This apparent lack of dilution or concentration is likely due to use of ratios rather than concentrations. Concentrations of both elements may have been affected similarly by growth, so that the ratios were unaffected.

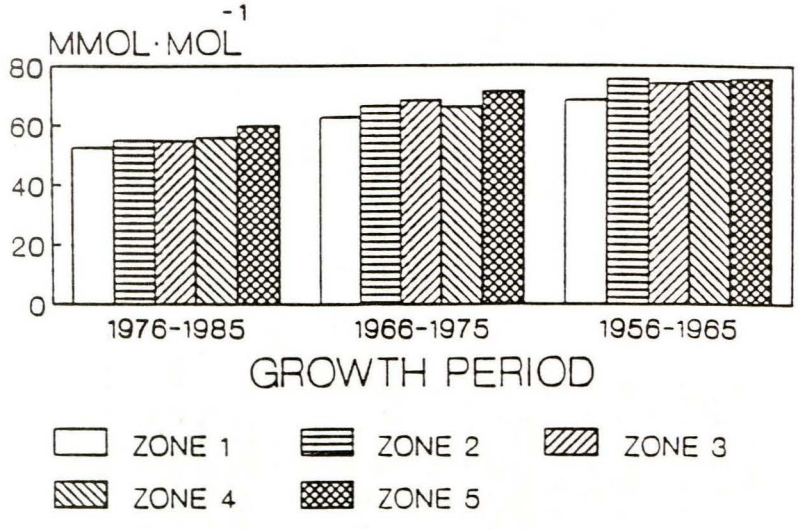

Figure 2.--Molar ratio of S to N for three growth periods for tree wood from zones 1 in northwestern Minnesota to 5 in southeastern Michigan. Differences among zones are significant for the 1976-1985 and 1966-1975 wood. Bayes LSD among the means are 5 mmol mol^{-1} for the 1976-1985 wood and 6 mmol mol^{-1} for the 1966-1975 wood (from Ohmann and Grigal 1990).

Differences in molar ratios among zones were significant for wood from both the 1966-1975 ($p < 0.03$) and 1976-1985 ($p < 0.02$) growth periods (Fig. 2) (Ohmann and Grigal 1990). In both woody increments, the molar ratios increased from west to east, from 52 to 60 mmol mol^{-1} in the 1976-1985 wood and from 63 to 71 mmol mol^{-1} for the 1966-1975 wood (Ohmann and Grigal 1990) (Fig. 2). In both cases, the BLSD indicated that the ratio for the westernmost zone (zone 1) was significantly lower than that in the easternmost zone (zone 5). These higher ratios in tree woody tissue from west to east along the gradient of deposition are consistent with the higher concentrations of S in soil from west to east.

LEAD AND CADMIUM IN FOREST FLOOR - ANALYSIS OF COVARIANCE

Analyses for metals in forest floor were done with ash as a covariate to adjust for variable inclusion of mineral soil material. Our analytical technique released elements bound within organic matter and on mineral and organic exchange sites. Varying quantities of ash (mineral matter) primarily influenced elemental concentration by affecting the unit dry weight of material. In our data only Mg and Na concentration were positively, albeit weakly, correlated with ash concentration ($r = 0.16$ and 0.20, respectively); increasing ash decreased concentration of all other elements. By using a covariate, all observations were converted to a common ash or mineral content.

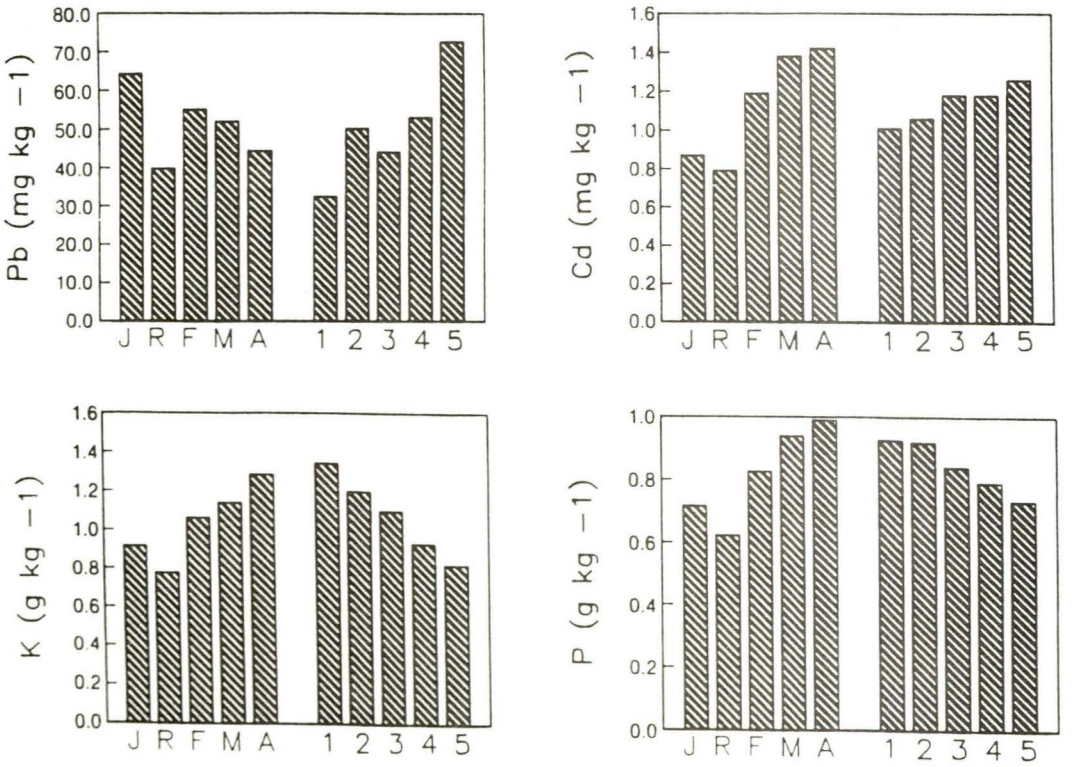

Figure 3.--Elemental concentrations in forest floor within five forest types and five geographic zones from 1 in northwestern Minnesota to 5 in southeastern Michigan. Data presented are means based on two-way ANOVA, using percent ash as a covariate (from Grigal and Ohmann 1989).

Ash was usually a significant covariate in the ANOVAs, as was zone (Grigal and Ohmann 1989). Elements in forest floor could be divided into three groups. One group (including Cu, Zn, and Ni) showed no geographic pattern in concentration. The second group included soil-derived elements such as K and P (and Ca, Mg and Na) (Fig. 3). They showed a general decline in concentration from west to east. The third group included Pb and Cd, and increased in concentration from west to east (Fig. 3). Although the ANOVAs indicated statistical significance for differences in Pb, they did not indicate such differences for Cd, but the linear trend of increasing means from west to east was significant ($r^2 = 0.94$, $p < 0.005$). These geographic trends are consistent with the presence of anthropogenic sources to the east, and parallel the patterns of other elements with known anthropogenic sources such as S.

MERCURY IN SOIL - SUBTRACTION OF BACKGROUND

Concentrations of Hg in forest floor showed the same trends of significant ($p < 0.0001$) increases from west to east as did the other atmospheric pollutants, with highest levels in zones 4 and 5. Although differences in Hg concentrations in mineral soil were also significant among zones ($p < 0.05$), trends were not as clear and mineral soil in zone 5, the most easterly zone, had lower concentrations. We were concerned about the influence of the geologic substrate. Our transect crossed highly variable geologic materials that were not uniformly distributed (Ohmann et al. 1989), and we did not expect a regular trend in Hg from that source. There was no significant difference among zones in concentrations of Hg in soil from the deepest horizon that we sampled, 76-100 cm ($p < 0.37$), but there was a close relationship between Hg concentration and silt plus clay content in that horizon ($r^2 = 0.74$, increasing to $r^2 = 0.88$ with deletion of an outlier). Using this relationship and silt plus clay in the surface soil, we estimated the geologic contribution ("background") of Hg in the surface.

We then calculated what can be defined as the net change in Hg mass for the surface soil by converting Hg concentrations to mass per unit area, and subtracting the background mass from that currently present. This net change significantly increased from the westerly to easterly zones ($p < 0.005$). Surface soils in the three westerly zones currently contain less Hg than background, indicating that Hg losses from that horizon have exceeded inputs. Soils in the two easterly zones contain 1.1 and 1.3 mg m^{-2} more Hg than background, indicating enrichment. When Hg mass in forest floor is added to the net change in the surface soil, all zones show net enrichment and a clear west-to-east trend, with highest net increases in the easternmost zones (Fig. 4). Based on current rates of atmospheric deposition in the region (ca. 15 μg m^{-2} yr^{-1}; Glass et al. 1991), this net enrichment represents 30 to 150 years of deposition, a reasonable range. The gradient in Hg enrichment is also consistent with the other gradients presented in this report.

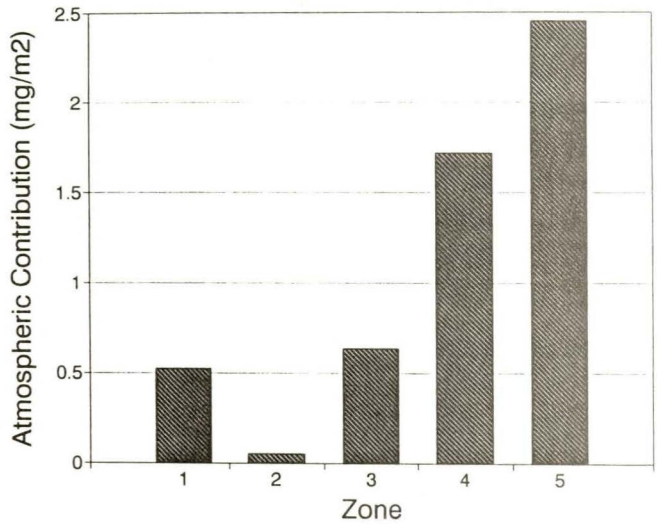

Figure 4.-- Estimated net Hg increase resulting from atmospheric deposition in five geographic zones from 1 in northwestern Minnesota to 5 in southeastern Michigan (from Nater and Grigal, unpublished).

CONCLUSIONS

This paper focused on terrestrial forest ecosystems in the northern Lake States. All of the studies reviewed here showed parallel patterns of elements considered to be atmospheric pollutants, with higher concentrations and amounts in eastern portions of the study area than in the west. Eastern portions of the area are also regions of greater industrial activity and atmospheric deposition of sulfur, a major atmospheric pollutant. A variety of techniques have been used to elucidate the trends because of the noise introduced by correlations among variables and by high native levels of some elements. These studies indicate that atmospheric deposition is differentially influencing forest systems in the northern Lake States.

ACKNOWLEDGMENTS

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MERCURY SPECIES IN LAKE WATER[1]

D. B. Porcella, C. J. Watras, N. S. Bloom[2]

ABSTRACT.--Atmospheric mercury participates in a global cycle. Apportioning emissions depends on a complex cycle involving transformations and transport. The key to understanding the mercury cycle is accurate data produced by clean sampling, handling and storage techniques coupled with robust and sensitive analytical procedures that measure individual species. These techniques have enabled mercury mass balances around remote lakes, analyses of deposition, and development of a mercury cycling model.

INTRODUCTION

Significant quantities of environmental mercury (Hg) cycle through air, water, and solid phases of the global environment. Current estimates place Hg cycling through the atmosphere at roughly 6 billion grams per year (Fitzgerald 1986, 1989). Natural sources and sinks for Hg have been identified in terrestrial, marine and freshwater ecosystems (Lindqvist et al. 1991, Fitzgerald et al. 1991, Watras et al. 1991). Mercury is important because the most toxic form, methyl-Hg, accumulates in aquatic life (Huckabee et al. 1979). Public concern stems from the tendency of methyl-Hg to bioconcentrate on the order of 10^6 to 10^7 in fish (Bloom et al. 1991) such that most of the methyl-Hg in small remote lakes resides within the fish community (Watras et al. 1991). Although mercury concentrations do not seem to affect aquatic organisms in the absence of gross contamination, birds, humans, and mammals that consume aquatic organisms may incur increased risks to health.

The global Hg cycle involves several biogeochemical transformations between inorganic and organic Hg species. Accumulation of mercury by organisms is strongly dependent on the Hg cycle. In turn the cycle depends on chemical form, subsequent chemical transformations, and

[1]Results in this paper come largely from the Mercury in Temperate Lakes (MTL) project supported by the Electric Power Research Institute (EPRI), Contract RP2020–10 and by the Wisconsin Department of Natural Resources. We gratefully acknowledge the contributions of many MTL investigators.

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interactions with organisms. Almost all atmospheric Hg is elemental Hg(0) (Fitzgerald et al. 1991, Lindqvist et al. 1991). In essence, wet deposition contains only forms of Hg(II), requiring that Hg(0) be oxidized before being stripped from the gas phase (Munthe, 1991).

Transformations in aquatic environments include methylation to methyl-Hg, demethylation, and reduction of Hg(II) back to Hg (0) (Lindqvist et al. 1991, Watras et al. 1991). Both biochemical and abiotic methylation have been implicated as sources of methyl-Hg (Jensen and Jernelov 1969, Wood et al. 1968, Lee et al. 1985). Dimethyl-Hg occurs in ocean waters (Mason and Fitzgerald 1990), but apparently not in fresh water environments. Both demethylation and reduction from Hg(II) to Hg(0) occur enzymatically; the Hg(0) escapes back to the atmosphere (Fitzgerald et al. 1991). Presumably, reductive processes occur on land, also, as land degassing of Hg(0) is a potentially important, but largely unquantified process (Lindberg et al. 1979).

Sources of atmospheric Hg include Hg(0) evasion from marine, freshwater, and terrestrial environments, combustion of fossil fuels containing trace amounts of Hg, and other anthropogenic sources. With a mean residence time of about one year, annual atmospheric input and deposition amounts to about 5-6 billion grams per year. Quantitatively, Fitzgerald (1989) estimated that the oceans emitted about a third, human activities produced a third, and by balance, the land a third of the total annual atmospheric input. Fitzgerald (1986) estimated that volcanos are a minor source. Atmospheric concentrations of Hg over the ocean surface in the northern hemisphere average almost double the southern hemispheric average, reflecting the increased anthropogenic activities concentrated above the equator. Depositional flux in the north exceeds southern hemisphere quantities significantly (Fitzgerald 1986).

Estimates suggest that up to half of the Hg directly entering the atmosphere from human activity arises from fossil fuel combustion (one-sixth of the global total), the remainder being other sources, such as paints, fluorescent lights, batteries, and cement manufacture. More recent estimates suggest higher emissions from fossil fuel combustion, up to half of the total global atmospheric input (Nriagu and Pacyna 1988), but these numbers include estimated emissions from eastern European countries which may or may not be accurate (Nriagu, Personal Communication).

The question of accuracy pervades all of these estimates of the Hg cycling. Without accurate and reproducible measurements, understanding of Hg cycling is impossible. Even small quantities can be environmentally significant, because Hg is bioconcentrated and biomagnified in aquatic food chains. For example, typical air concentrations are 1-2 ng/m^3 (about 1-2 ng/kg), and typical water concentrations are 0.5 to 2 ng L^{-1}. Analytical procedures must be sensitive and robust to measure these quantities routinely (Fitzgerald and Gill, 1979, Bloom and Fitzgerald, 1988, Bloom, 1989), and laboratory and sampling techniques must utilize clean sampling/handling protocols (Fitzgerald and Watras 1989, Watras et al. 1990). Some recent compilations from the Mercury in Temperate Lakes (MTL) project show that improvements in laboratory cleanliness improve estimates of Hg in lake water, but substantial improvements occur with both clean lab and clean sampling techniques combined (Fig. 1). Similarly, results improve for all of the trace metals with combined clean lab and sampling techniques (Fig. 2). We cannot overstress the importance of clean techniques.

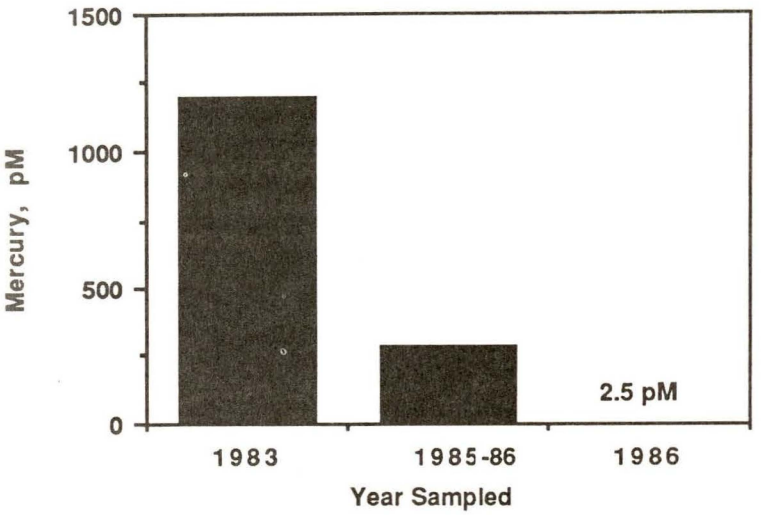

Figure 1.-- Estimates of Hg concentrations in Vandercook Lake, WI have decreased with time as investigators adopted progressively cleaner techniques for sample collection and handling (Fitzgerald and Watras 1989).

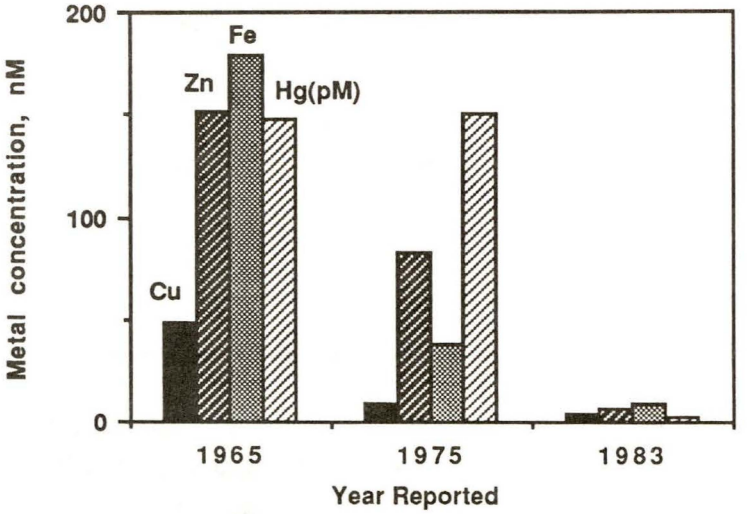

Figure 2.-- Concentrations of several trace elements in ocean waters have decreased with time as clean techniques became more widespread (Fitzgerald and Watras 1989).

Documented cases of sample contamination illustrate some of the difficulties that may arise. For example, one of our 'rigorously cleaned' sampling devices often but not always gave higher Hg concentrations than other samplers. With field samples the overestimates from this sample ranged from about 0.5 to 1.5 ng L^{-1}. We did not know if the problem was operator-related or intrinsic to the sampler. We detected no contamination in short laboratory tests. Longer exposures using low-Hg water and subsampling revealed that Hg concentrations increased linearly at a rate of about 1.5 ng L^{-1} hr^{-1} due to leaching of Hg from some component of the bottle, even though the bottle and messenger had been Teflon^{R}-coated and rigorously acid-washed (Fig. 3). Given sample handling times in the field, the leaching could double the estimated concentrations in the MTL study lakes. A similar bias can result from improper storage in the laboratory. Gaseous Hg in indoor air can readily contaminate samples (Gill and Fitzgerald 1987).

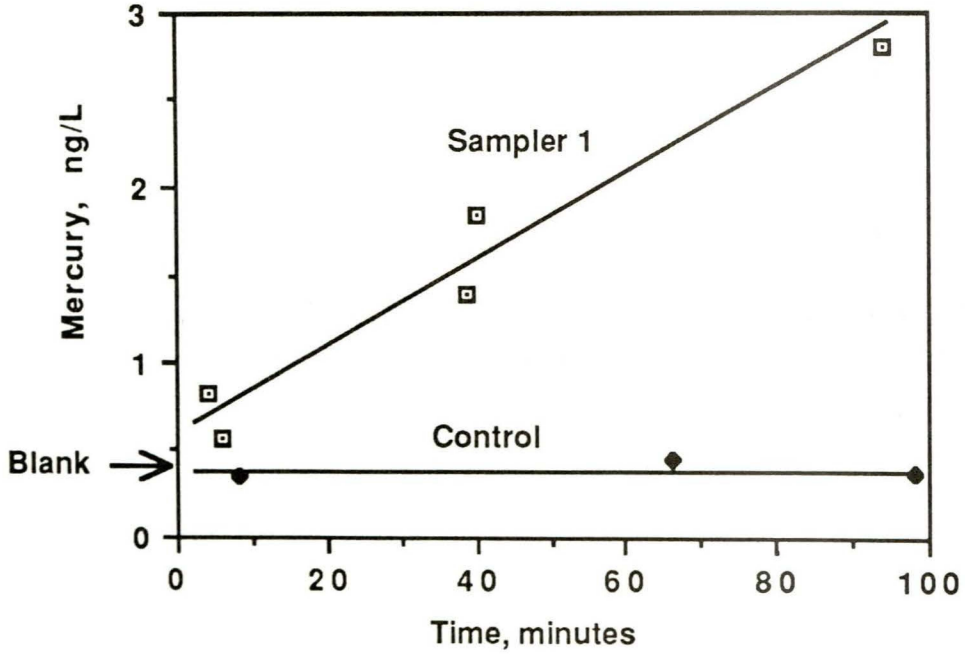

Figure 3.-- Hg leaching from a rigorously cleaned sampler into low-Hg water (ca. 0.3 ng L^{-1}). Data generously provided by Grace Vandal, University of Connecticut (after Watras et al. 1990).

Interlaboratory comparisons are prerequisite to assuring high quality Hg data. Table 1 illustrates the results of a comparison between three groups analyzing replicate samples from a lake in California. This particular comparison only addresses handling and analytical protocols, since one group collected the sample and split it among the investigators. Adequately low detection limits are also a prerequisite to Hg analysis in natural water samples (Table 2).

Table 1.-- Three-laboratory intercomparison for total Hg in a filtered surface water sample from Davis Creek Reservoir. (See Gill and Bruland 1990 for description of the reservoir.)

	Hg (ng L^{-1})		
Rep. No.	BRL[1]	UCSC[2]	UCONN[3]
1	1.94	1.86	2.00
2	1.98	1.89	1.90
3	2.47	2.38	1.60
4	no data	1.88	1.70
Mean	2.13	2.00	1.80
SD	0.30	0.25	0.18

[1] BRL-Brooks Rand LTD (N. Bloom); [2] USSC-UC Santa Cruz (G. Gill); [3] UCONN-University of Connecticut (W. Fitzgerald).

Hg concentrations in pristine lakes where clean lab and sampling techniques coupled with low analytical detection limits produced accurate measurements of Hg in water are listed in Table 3. Lakes receiving known Hg sources differ markedly from those with no known input other than

Table 2.-- Typical detection limits (1 SD of triplicate blank analyses) and ambient concentrations for Hg species in lake water samples. Volumes and detection are limits based on filter clogging (0.8µ quartz fiber filter).

Hg Species	Sample size (mL)	Detection limit (ng L^{-1})	Typical pristine waters (ng L^{-1})
Total	100	0.05	1.0
Acid labile[1]	100	0.002	0.05
Elemental	2000	0.00005	0.02
Particulate total	1000	0.02	0.2
Complexed organic	100	0.08	0.8
Total methyl	50	0.004	0.05
Dimethyl	1000	0.0001	<0.0001
Labile methyl	50	0.002	0.02
Particulate methyl	1000	0.005	0.04

[1] Acid labile in high DOC freshwaters may be inaccurate.

atmospheric deposition and natural runoff. Investigators should look for sources of contamination when values exceed the ranges encompassed by the remote lakes listed in Table 3. Contamination may arise from an undiscovered point source, or from improper laboratory or sampling procedures. Results for a broader range of lakes, some with Hg waste point sources, exhibit higher concentrations (Gill and Bruland 1990), but even so, do not exceed 6 ng L^{-1}.

Table 3.-- Wisconsin lakes where clean techniques were used to sample and analyze Hg during the Hg in Temperate Lakes project. (Data are volume-weighted, whole-lake average concentrations from Watras et al. 1991.)

Lake name	Total Hg (ng L^{-1})
Little Rock Treatment[1], 1988	1.18
Little Rock Treatment[1], 1990	1.29
Little Rock Reference[1]	1.22
Vandercook Lake	1.02
Max Lake	0.90
Crystal Lake	0.97
Russet Lake	2.30

[1] Little Rock Lake was physically divided into two areas to acidify one side (treatment) and use the other side (reference) for comparison (Watras and Frost 1989).

Even lakes located in the same geographic area show small but significant differences in concentrations of Hg that seem to be associated with specific water chemistry constituents (Fig. 4). Although environmental Hg concentrations are very low, significant differences occur between lakes that span gradients of pH and DOC (Watras et al. 1991). Similar differences in fish Hg have been reported (Wiener 1987, Grieb et al. 1990, Lathrop et al. 1991). The mechanism for associations between increased Hg in fish and low pH or different DOC remain unexplained, but recent data on partitioning of methyl-Hg between water and particulates in these remote, clean, dilute water lakes suggests that these variables may have a stronger effect on methylation than on specific uptake rates by organisms (Bloom et al. 1991) (Fig. 5).

Using clean techniques, the MTL project has obtained the first mass balances for total Hg and methyl-Hg in remote lakes (Fitzgerald and Watras 1989, Wiener et al. 1990, Watras et al. 1991). Results show that atmospheric deposition can account for virtually all the annual lake Hg input to seepage lakes (Watras et al. 1991). Although methyl-Hg has been identified in precipitation, atmospheric deposition is less important than internal generation as a source to the Wisconsin study lakes (Bloom and Watras 1989, Fitzgerald et al. 1991). Moreover, oceanic measurements of atmospheric Hg concentrations and Hg deposition in the northern hemisphere do not differ substantially from values for Northern Wisconsin or for the Olympic Peninsula, Washington. This result suggests that Hg has a global cycle that controls deposition in many remote areas. We expect that emissions of Hg (II) or of materials that oxidize Hg (0) to Hg (II) would lead to locally elevated deposition of Hg (Fitzgerald et al. 1991, Munthe, 1991). However, little evidence of elevated Hg deposition at local sites has so far been obtained.

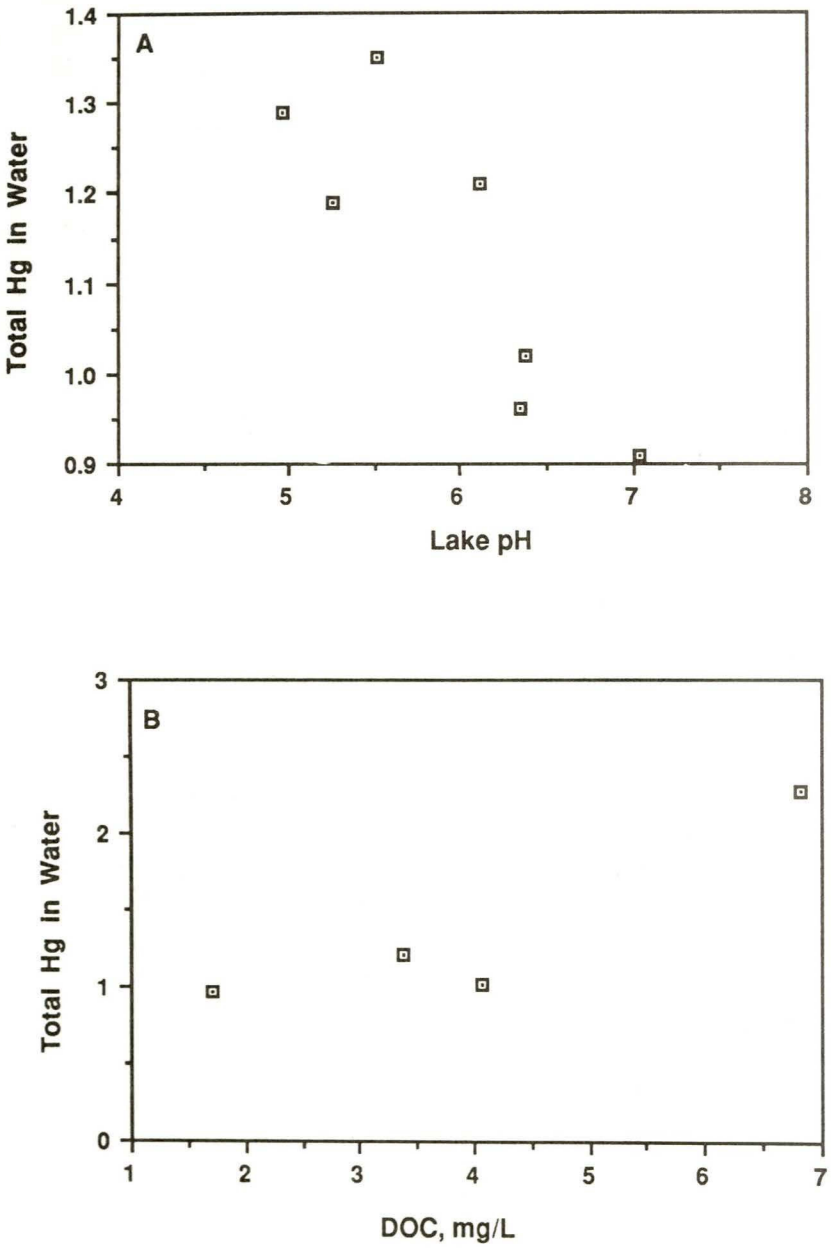

Figure 4.-- Hg concentration (ng L^{-1}) in lakewater as a function of pH (A) and DOC (B) in selected seepage lakes in Northern Wisconsin. Data from Watras et al. 1991.

In contrast to air and water, fish and sediment act as sinks for Hg. Concentrations of Hg are high enough in fish and sediments so that extremely clean techniques are not required to obtain reliable measurements. In fact, fish and sediment samples should not be analyzed in clean labs used for air and water trace chemical analyses without stringent precautions.

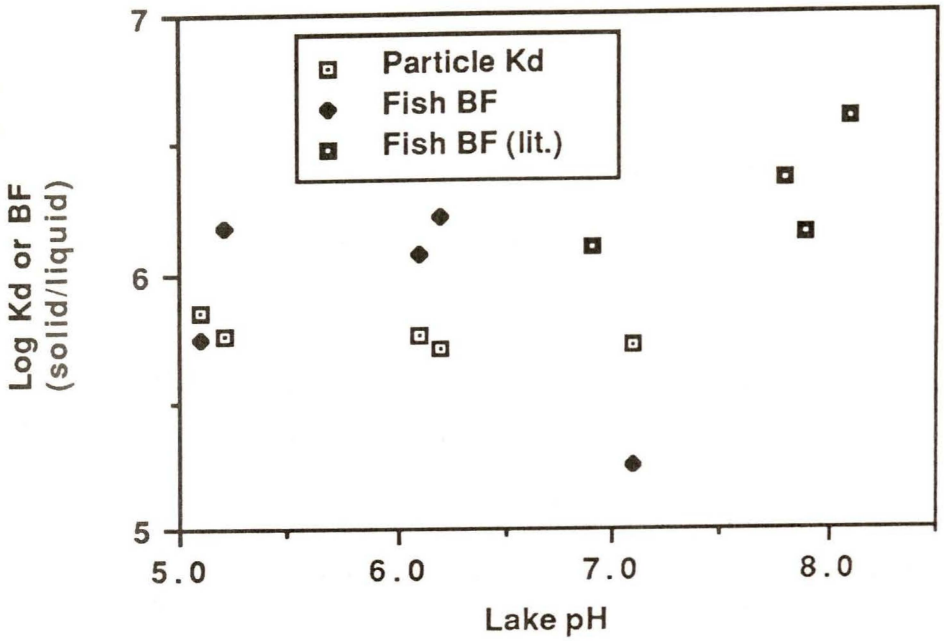

Figure 5.-- Partition coefficients (Kd) and bioconcentration factors (BF) for methyl-Hg in age-1 yellow perch and bulk seston (mainly phytoplankton) in Northern Wisconsin lakes spanning a wide range of pH (from Bloom et al. 1991).

The Mercury in Temperate Lakes project developed the mercury cycling model to predict fish mercury concentrations in lakes receiving different amounts of the different species of mercury (Hg(II), Hg(0), methyl-Hg, strongly complexed Hg) (Hudson et al. 1990). At present the Hg cycling model simulates aggregated sources from atmospheric deposition and surface and ground water inflows. The model would not be possible if accurate data on precipitation, water, and air concentrations were not obtainable to parameterize the relationships. The task of confirming model predictions of fish Hg remain to be accomplished. Note that model predictions are consistent with field data; for example, Gill and Bruland (1990) showed that the fish integrated Hg accumulation relates well to estimates of aqueous methyl-Hg. In fact, fish have historically been better collectors of aqueous methyl-Hg than humans.

CONCLUSIONS

1. Understanding the global Hg cycle requires the measurement of Hg in some large but very dilute pools (i.e. air, water, precipitation).

2. Concentrations are so low (picomolar) that extreme care in sample collection, handling, and storage are required to avoid contamination and the generation of large errors in the data set.

3. As a result, much of the data collected without clean techniques has been misleading.

4. The process of Hg bioaccumulation requires the formation of methyl-Hg species within the ecosystem. Thus, novel analytical techniques have been developed to measure methyl-Hg at very low environmental concentrations.

5. The application of Hg-clean sampling protocols and novel analytical techniques has permitted us to formulate a mass balance for Hg and methyl-Hg in a remote lake ecosystem. This mass balance serves as the basis for the Mercury Cycling Model and for process level investigations currently underway.

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ATMOSPHERIC CYCLING AND AIR-WATER EXCHANGE OF MERCURY OVER MID-CONTINENT LAKES[1]

W.F. Fitzgerald, R.P. Mason and G.M. Vandal[2]

ABSTRACT. Atmospheric mobilization, and exchange at the air-water interface are significant features of biogeochemical cycling of Hg at the Earth's surface. We are investigating the tropospheric cycling, deposition and air-water exchange of Hg in the mid-continent lakes of northcentral Wisconsin. We have found Hg concentrations and atmospheric fluxes in these fresh water systems to be similar to open ocean regions in the Northern Hemisphere. A well constrained mass balance for Hg, developed for Little Rock Lake, shows that the measured total atmospheric Hg deposition (ca. 10 $\mu g\ m^{-2}\ yr^{-1}$) readily accounts for the total mass of Hg in fish, water and accumulating in the sediments of this lake. This analysis demonstrates the importance of atmospheric Hg to the geochemical cycling and bioaccumulation of Hg in temperate lakes. It further suggests that modest increases in atmospheric Hg could lead directly to enhanced levels of Hg in biota. Analogous modeling for monomethylmercury (MMHg), while limited, indicates that this flux is insufficient to account for the amounts of MMHg observed in biota. An in-lake synthesis of MMHg is implicated. The importance of volatile Hg, principally elemental Hg (Hg^o), and its evasion to the atmosphere is also illustrated. We suggest that the in-lake production of Hg^o can reduce the Hg (II) substrate used in the in-lake microbiological synthesis of MMHg.

INTRODUCTION

Mercury in the environment continues to be the focus of much scientific inquiry and public debate. The three phase nature of its biogeochemical interactions and cycling presents a substantial investigative challenge. Human health concerns are pronounced because Hg and certain of its compounds, e.g., monomethyl Hg (MMHg), accumulate in biota particularly in larger fish. This problem is quite complex because MMHg, the principal species in fish, is more toxic than inorganic Hg and produced principally by *in situ* biologically mediated transformations

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of Hg species (Westöö 1966, NAS 1978). The human health issue is further complicated by the potential amplification of Hg within the ecosystem due to Hg emissions and discharges associated with a variety of human endeavors. Of particular concern is the dispersion and deposition of Hg through the atmosphere. The preeminence of atmospheric pathways for the mobilization of Hg at the surface of the earth is well established (Wollast et al. 1975, NAS 1978, Slemr et al. 1981, 1985, Fitzgerald et al. 1981, 1983, Lindqvist and Rodhe 1985). Recent investigations place the total annual Hg flow through the atmosphere in the 5-7 x 10^9 g range (Slemr et al. 1981, Fitzgerald et al. 1981, Fitzgerald 1986, Nriagu 1989). This refined estimate is much smaller even than the natural or "pre-industrial" fluxes proposed in many earlier models. Accordingly, current estimates place the range of anthropogenic interferences at between 30% and 60% of the total annual Hg deposition (Fitzgerald 1986, 1989, Nriagu and Pacyna 1988). Further, it is becoming increasingly evident that a relatively modest interference of human-related emissions on the background levels of atmospheric Hg could translate into Hg levels in organisms that are of ecologic and perhaps toxicologic concern.

We have extended our investigations of the tropospheric chemistry and oceanic cycling of Hg to terrestrial aquatic systems where we are studying the atmospheric cycle, air-water transfer and exchange of Hg in the temperate mid-continent lakes of northcentral Wisconsin. This study is part of a multidisciplinary examination of the processes regulating the aquatic biogeochemistry of Hg in these natural waters. Trace-metal-free procedures are used to measure Hg and alkylated Hg species at the picomolar level in air, water, biota and precipitation. We have found the various compartments in these aquatic systems to have Hg concentrations that are often similar to pristine open ocean regions of the northeast Pacific Ocean. Here we present initial results from our studies of the atmospheric cycling and water-air exchange of Hg in this mid-continent aquatic environment. We have been able to generate a well constrained mass balance for Hg at one of the lakes, Little Rock Lake, which shows that the measured total atmospheric Hg deposition (ca. 10 $\mu g\ m^{-2}\ yr^{-1}$) readily accounts for the total mass of Hg in fish, water and accumulating in the sediments. These results confirm the preliminary mass balance for the biogeochemical cycling of Hg in this lake (Fitzgerald and Watras 1989, Wiener et al. 1990).

High concentrations of Hg are present in piscivorous fishes from low alkalinity lakes in these environs. Rada et al. (1989) reported an increase in atmospheric Hg deposition of a factor of 3 or 4 since precolonial times as inferred from analyses of lake sediment cores. Moreover, even the present yearly remote oceanic deposition of Hg when normalized to a square meter basis at about 4-7 $\mu g\ m^{-2}\ yr^{-1}$ (Fitzgerald and Gill 1985, Gill and Fitzgerald 1987) would introduce an annual amount of Hg comparable to the total Hg burden present in the water and biota of many freshwater lakes. In addition, hemisphere wide increases in Hg deposition appear implicated by the current geographically broad pattern (e.g. Canada, U.S., Sweden) of elevated Hg levels found in fish even in watersheds far from anthropogenic sources (Wiener 1987).

This analysis also demonstrates the importance of atmospheric Hg to the geochemical cycling and bioaccumulation of Hg in temperate seepage lakes, and the potential linkage between modest increases in atmospheric Hg loading and enhanced Hg levels in biota. The speciation data suggest that (1) atmospheric deposition of MMHg is an inadequate source for the amounts of MMHg observed in biota; (2) the bioaccumulation of Hg as MMHg in biota may be directly related to

the in-lake availability of Hg (II) substrate for methylation, and (3) we hypothesize that the in-lake production of volatile Hg which is principally the elemental form (Hg^{o}), and its evasion to the atmosphere can reduce the Hg (II) substrate and the concomitant microbiological synthesis of MMHg.

EXPERIMENTAL

STUDY REGION

This multi-discipline biogeochemical investigation of Hg has focused on representative clear-water seepage lakes in the Northern Highland Lake District of Wisconsin, near Trout Lake in Vilas County (46°00'N, 89°40'W). The region is sparsely populated, lacks heavy industry, and the land area is nearly 90% forested. The lakes in the study are moderately productive (oligiotrophic-mesotrophic) and were selected to span a range of pH (4.7 to 7.2), ANC (15 to 128 $\mu eq\ L^{-1}$) and dissolved organic C (1.5 and 5.6 $mg\ L^{-1}$). These parameters have been correlated with the bioaccumulation of Hg in natural waters (Scheider et al. 1979, Hakanson 1980, Sloan and Schofield 1983, Lindqvist et al. 1984, Wiener 1987). Additional information on the region and many of its lakes can be found in Eilers et al. (1983), Magnuson et al. (1984), Watras and Frost (1989), and Vandal et al. (1991).

One of the study lakes, Little Rock Lake (LRL) has been divided with a sea curtain into two basins, one of which is untreated (reference pH: 6.1; LRLR) while the other is being experimentally acidified with H_2SO_4 (current pH: 4.7; LRLT) starting after ice-out in the early spring of 1985 (Watras and Frost 1989). The reference basin has not been acidified. The two basins had very similar chemical composition (mean pH 6.1, alkalinity 26 $\mu eq\ L^{-1}$, specific conductance 12 $\mu S\ cm^{-1}$) and biota at the start of the experimental acidification (Brezonik et al. 1986). The lake receives > 95% of its water from direct precipitation and its watershed is uninhabited, state-owned, and completely forested (Watras and Frost, 1989). Our air and precipitation collection stations are located on the reference side. Additional information on the Little Rock Lake Acidification Project can be found in Magnuson et al. (1984), Brezonik et al. (1986), Watras and Frost (1989), and Fitzgerald et al. (1991).

ANALYTICAL

Air collections for Hg have been made using a battery operated modification of the atmospheric sampling systems we developed and used successfully in oceanic studies (Fitzgerald and Gill 1979, Fitzgerald, 1986, 1989). The apparatus was installed on a US Geological Survey meteorological raft centrally located on LRLR. This site was most suitable, since localized contamination was reduced. The air was sampled upwind as the raft acted as a sail orienting the collection apparatus windward. During the ice season, the raft was located on the shore. The atmospheric Hg sampling stacks consist of the following trapping materials: Au (yields a total gaseous Hg determination (TGM)); Carbotrap^{R}/Au (provides a collection that can be used for direct Hg speciation determinations); Quartz wool plug (for particulate Hg determinations (PM)). Additional details associated with these various trapping materials can be found in Fitzgerald and

Gill (1979), Kim and Fitzgerald (1986) and Bloom and Fitzgerald (1988). Samples for total gaseous Hg (TGM), particulate Hg (PM) and speciation of the gaseous phase (CTS) were collected at Little Rock Lake by personnel from the Wisconsin Department of Natural Resources (WDNR), and shipped to the University of Connecticut (UCT) for analysis. Samples volumes ranging between 0.5 and 2.0 m^3 were collected over a 24 hour period.

The TGM analyses are conducted by the two-stage gold amalgamation technique (Fitzgerald and Gill, 1979) with detection by atomic fluorescence spectroscopy (AFS). Currently, the overall TGM methodology has a detection limit of ca. 0.15 ng m^{-3} and a precision of ca. 15% at 1.5 ng m^{-3}. Particulate Hg is determined following pyrolysis of the quartz wool plug and trapping on gold. Chemical speciation of the gaseous phase is achieved through analysis of the graphitized substrate (Carbotrap^R) collections using gas chromatographic separation and AFS detection (Bloom and Fitzgerald 1988). The detection limit for the determination of MMHg and dimethylmercury (DMHg) is ca. 5 pg m^{-3}.

All rainfall is collected on an event basis by WDNR personnel and ultra-clean protocols are employed. The rain collection apparatus are placed on a small platform on the shore at LRLR. One device, previously used in open ocean studies, consists of a large custom made pyrex glass funnel (approx. 45 cm diameter), that is contained in an open Al frame. The other collector is a solid Teflon^R machined funnel with a threaded adapter for the collection bottles (Mason et al. 1991). Both collection devices are fitted with threaded Teflon^R unions that insure that no leakage occurs and contaminated rain (e.g. rain (splash) that has contacted the apparatus) cannot enter the collection bottle. The funnels are deployed at the beginning of a rain and are rinsed with 1-L of clean acidified water (1% HCl). A second 1-L aliquot of water is used to take a funnel blank. Half of the aliquot is rinsed through the funnel and collected and the other half is retained without passing through the funnel. These samples are used to test and monitor the funnels for artifacts and potential contamination. The funnel is exposed to the atmosphere for the duration of the event. Following the sampling, the rain collectors are carefully put away. An aliquot of rain for ethylation/speciation determinations is decanted into a 100 mL bottle prior to sample acidification. The 100 mL aliquot is frozen and shipped separately to the UCT for analysis.

Snow is carefully collected into 1-L acid-cleaned Teflon^R jars, sealed and shipped to UCT frozen and without acidification. Great care is taken to maintain sample integrity during collection and shipment. During snow collection operations, the sampling personnel wear particle-free nylon suits (reserved for snow collection) and use arm-length plastic gloves. Snow is carefully scooped into the clean Teflon^R jar. Particular attention is given to the wind direction to prevent particles blowing into the sample from personnel or equipment. The sampling equipment is transported on sleds drawn by the collectors who walk to the sampling area. This difficult procedure reduces potential contamination associated with gasoline powered machinery. In general, freshly fallen snow is collected from the reference basin of Little Rock Lake near the deepest part of the lake. One particular snowfall was sampled twice, once just after stoppage and again 5 days later. The analyses show the enhanced Hg concentration in surficial snow due to dry particle Hg deposition over the 5 day period (see Figure 3). The snow samples for reactive Hg and total Hg determinations are acidified with analyzed reagent grade HCL in our class 100 clean laboratory,

resealed and allowed to thaw at room temperature. The sample for chemical speciation is allowed to thaw without acidification. The samples are analyzed immediately after thawing.

Three different procedures are used in the analysis of rain and snow samples and the measurements obtained provide information on the forms of Hg in precipitation. All methods rely on the production of volatile Hg species in solution which are purged from solution with inert, Hg-free gas and trapped on adsorbing substrate. The determination of "reactive" or "acid-labile" Hg (Hg_R) involves sample acidification to pH 1, reduction of ionic Hg and labile Hg to Hg^o with $SnCl_2$, aeration of the solution and collection on Au (Gill and Fitzgerald, 1987a). The determination of "total" Hg (Hg_T) is similar to the reactive Hg procedure after sample pretreatment with a strong oxidant, BrCl, followed by reduction of the BrCl with NH_2OH-HCL, prior to $SnCl_2$ reduction, aeration and collection on Au (Bloom and Crecelius, 1983). Oxidation of the solution with BrCl will destroy many strong organo-metal associations and decompose MMHg rendering bound Hg available for $SnCl_2$ reduction. The procedural blank for the reactive Hg determination is 0.025 ng ± 0.010 ng and the sample size is generally 250 mL resulting in a detection limit (defined as 3 x the standard deviation of the blank) of 0.5 pM. The blank associated with the oxidation technique is 0.1 ng ± 0.03 ng for a 250 mL sample with a corresponding detection limit of 2 pM.

Quantification and identification of Hg species in precipitation has been quite successful. The technique involves the ethylation of dissolved Hg in solution using sodium tetraethylborate. The volatile ethyl-Hg derivatives, as well as other volatile Hg species in solution (i.e Hg^o and dimethylmercury), are purged from solution, concentrated on Carbotrap^R, separated by cyrogenic GC and detected by atomic fluorescence. The details of the procedure are outlined in Bloom (1989). This method allows for the identification and measurement of MMHg, as methylethylmercury, labile Hg(II), as diethylmercury, and DMHg and Hg^o without ethylation. The detection limits are 0.05 pM for MMHg, and 0.1 pM for Hg(II).

LAKE WATER: DISSOLVED GASEOUS MERCURY

Details associated with our investigations of the cycling of volatile Hg can be found in Vandal et al. (1991). Briefly, intensive experiments were conducted at LRL in October, 1988 after fall overturn. LRLR, LRLT, Max, Vandercook (VDC) and Pallette (PAL) lake were studied during late winter/ice conditions (March, 1989). These five sites were reexamined in August, 1989, during summer stratification. Water was collected by hand with a 8-L Teflon^R coated Go-Flo^R sampling bottle using Kevlar^R line, a Teflon^R weight and messenger. The bottle integrates ca. 1 m depth range. Sampling was conducted from a fiberglass boat except in March, 1989 when we sampled through the ice. Usually, one site was sampled on a given day and the water analyzed immediately upon returning to the clean laboratory (ca. 1 to 3 hr) at the U. of Wisconsin Limnological Center at Trout Lake. The samples were maintained near their ambient temperature until analysis.

Dissolved gaseous mercury (DGM) measurements are made by sparging the volatile species from solution using Hg-free argon and trapping on either Au or Carbotrap^R (CTS) without pretreatment

of the sample. The collection of Hg on Au allows for the measurement of total DGM and the CTS collection allows for separation and identification of the volatile dissolved species by cryogenic GC with AFS detection. The samples were purged in a 2-L pyrex bubbler, and a total sample volume of 4-L was used for each determination. The detection limit for total DGM is 5fM (femtomolar) and 3fM for DMHg.

RESULTS

ATMOSPHERIC CYCLING OF MERCURY

In Figure 1, we have summarized the Wisconsin TGM data as well as results from a variety of studies at differing geographic locations from the remote ocean atmosphere to coastal and urbanized areas. The atmospheric TGM data and Hg speciation results show several significant features. The major observations are as follows: TGM consists principally of Hg° (> 99%) and the concentrations are in the range found over the remote North Central Pacific Ocean where TGM varied between 1.47 and 2.17 ng m^{-3} with an average of 1.77 ±0.15 ng m^{-3} (n = 47). The Wisconsin studies (1988-90) have yielded a range of TGM between 1.00 and 2.45 ng m^{-3} with an average of 1.50 ± 0.38 ng m^{-3} (n = 48) (Table 1). There is no strong evidence for continental sources of Hg. Figure 1 illustrates the anomalously interesting position of the Wisconsin site. To date we have not observed values of TGM approaching 3 ng m^{-3} as one might anticipate from the other investigations. Table 1 summarizes the Wisconsin atmospheric data. The major form of Hg in the atmosphere is elemental. Our studies have found that MMHg concentrations in the gaseous phase are generally less than the detection limit (Table 1). These findings are consistent with the quantities of MMHg measured in precipitation.

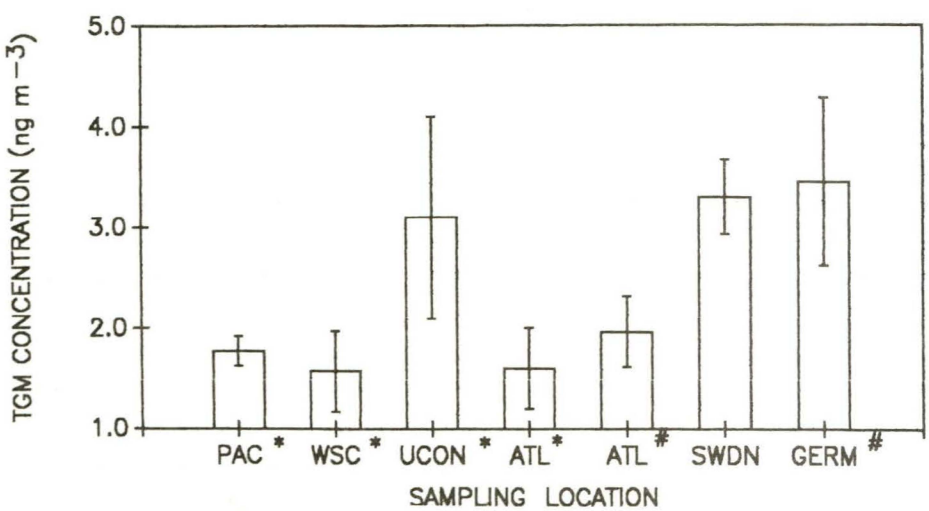

Figure 1.--Total gaseous Hg concentrations at various locations in the Northern Hemisphere [*Fitzgerald 1989 (northeast Pacific (PAC), northwest Atlantic (ATL) and Long Island Sound (UCON)); WSC = Little Rock Lake; #Slemr et al. 1985 (North Atlantic and Germany); SWDN = Sweden (Brosset 1982)].

The atmospheric particulate Hg determinations from LTLR are summarized in Tables 1 and 2. Additional data from our studies of Hg associated with particulate matter in the air at Avery Point, Connecticut, and measurements from our open ocean studies are also included. While there is significant short time scale variability associated with the terrestrial measurements, the average concentrations provide a consistent pattern where the mean values (62 ± 48 pg m^{-3}) from the coastal urbanized Connecticut region are greater than the midcontinent rural LTLR data (22 ± 19 pg m^{-3}). Open ocean atmospheric particulate Hg concentrations from trade wind locations (Enewetak Atoll; American Samoa) and the South Pacific Westerlies ranged between 0.4 and 2.0 pg m^{-3}. As anticipated there is a significantly greater decrease in particulate Hg concentrations relative to TGM from the terrestrial environs to the open ocean.

It is difficult to quantify the contribution of dry depositional fluxes of Hg to the midcontinental lacustrine region because of the lack of size distribution information. However, an average flux can be derived by using the mean particulate Hg concentrations in Wisconsin of about 22 ± 19 pg m^{-3}, and a representative deposition velocity of 0.5 cm s^{-1} (GESAMP Working Group 14, 1989). An average depositional flux of 3.4 ± 3.0 μg m^{-2} yr^{-1}

Table 1. Summary of atmospheric gaseous Hg data collected in Wisconsin between May 1988 and August 1990.

Hg SPECIES	SAMPLE #	RANGE (ng m^{-3})	AVERAGE (ng m^{-3})	% OF TOTAL
Hg^{o}	48	1.00-2.45	1.50 ± 0.38	98.0
MMHg	42	<0.005-0.038	<0.005	<0.3

is obtained. This is a geochemically significant flux of Hg from the atmosphere. Moreover, on shorter time scales, this flux may vary over an order of magnitude. During an intensive two-week study in August, 1989, for example, the particulate concentrations ranged from 7 to 62 pg m^{-3}. These concentrations would correspond to daily depositional Hg fluxes between 3 and 27 ng m^{-2} day^{-1}. This short-term variability further emphasizes the importance of particulate Hg loading to natural waters and the need for good particulate measurements.

Rain collections were made from May - August, 1989 at the LRLR sampling site. The results are summarized in Figure 2. The total Hg concentrations which range from 3.2 to 15.2 ng L^{-1} (10.5 ± 4.8 ng L^{-1}) are quite reasonable. Indeed these concentrations are similar to values for rains over the northeast Pacific (9 ± 5 ng L^{-1}; Fitzgerald 1989). Moreover, these levels are expected from a consideration of the observed concentration range of atmospheric particulate Hg and the expected rainfall scavenging of this Hg bearing particulate material (Fitzgerald et al. 1991, Mason et al. 1991).

Table 2. Atmospheric particulate Hg concentrations.

LOCATION	DATE	SAMPLE #	RANGE Hg Conc. (pg m^{-3})	MEAN and Std. Dev. (pg m^{-3})
Little Rock Lake, WI	Mar. to Aug., 1990	34	5 - 82	28 ± 23
Long Island Sound, Avery Point, CT	Dec., 1988; Jan. and June, 1989	22	5 - 180	62 ± 48
Pacific Ocean	1981-1983	7	0.4 - 2.0	--

An estimate of the annual deposition of total Hg in rainfall was made by combining the total Hg (average and S.D. of 10.5 ± 4.8 ng L^{-1}) with the observed total rainfall (42.4 cm yr^{-1}) measured by Trout Lake Laboratory personnel from September 1988 to September 1989. This calculation yields an estimate of the yearly deposition of total Hg of 4.5 ± 2.0 μg m^{-2} yr^{-1}.

The total Hg determinations in snow (Fig. 3) show slight variability. The average total Hg concentration was 6.0 ng L^{-1} with a S.D. of 0.9 ng L^{-1} . Annual total Hg deposition was estimated using the average quantity of total Hg and the observed total snowfall (37.6 cm yr^{-1}) measured by Trout Lake Laboratory personnel from September 1988 to September 1989. This calculation yields an estimate of the yearly deposition of total Hg in snowfall of 2.3 ± 0.3 μg m^{-2} yr^{-1}.

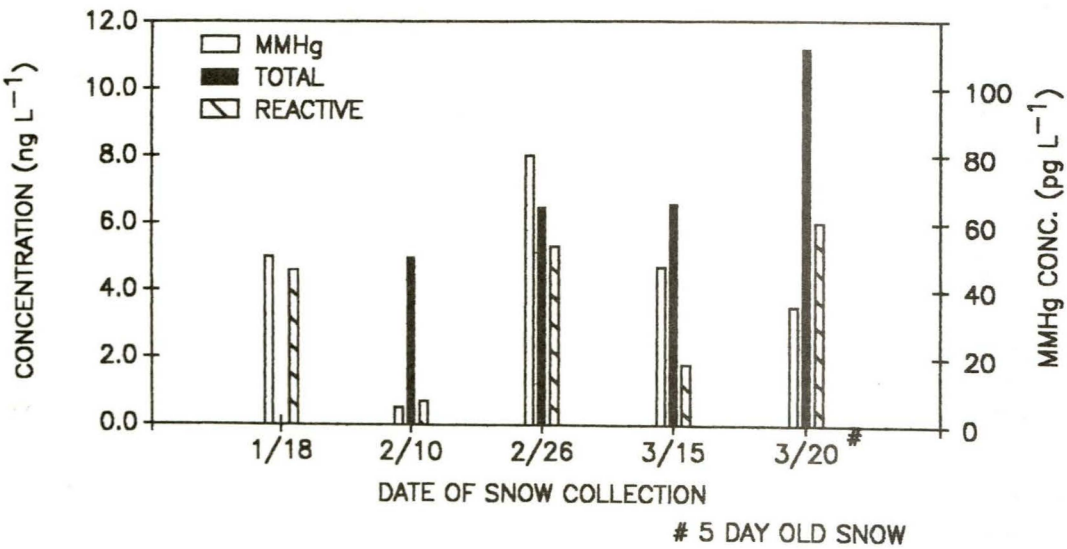

Figure 2. Mercury species [MMHg, Hg_R and Hg_T] in rain at Little Rock Lake, WI, 1989.

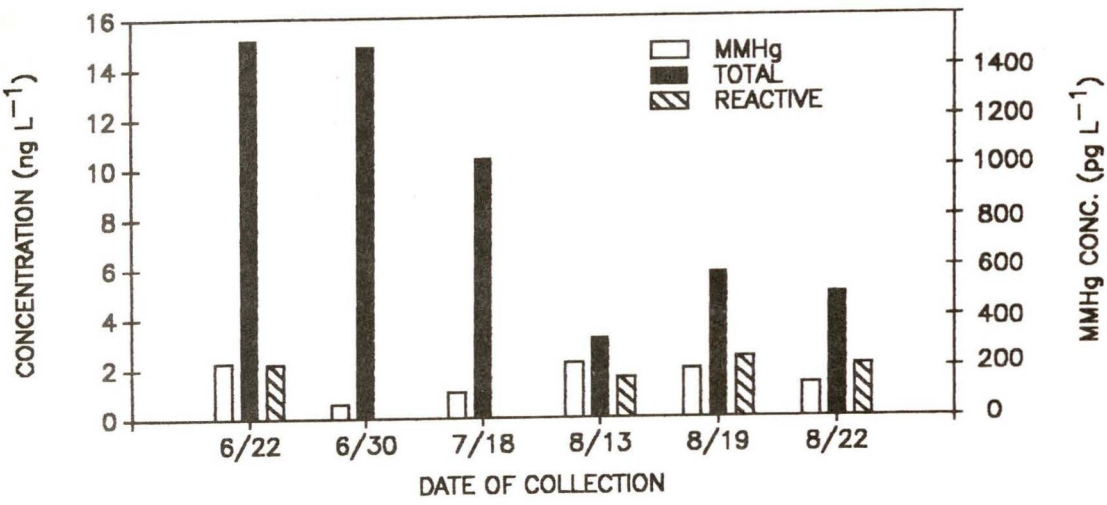

Figure 3. Mercury species [MMHg, Hg_R and Hg_T] in snow collected at Little Rock Lake, WI, 1989. Five day old snow denoted by #.

The results for the speciation of Hg in precipitation are most interesting geochemically (Figs. 2 and 3, respectively). Firstly, and though the measurements are limited, the difference between the Hg_R and Hg_T concentrations is striking. The Hg_R fraction, which consists principally of divalent Hg (II) species varied from 1.6 to 2.3 ng L^{-1} with an average of 2.0 ± 0.3 ng L^{-1} in rain and between 0.7 and 5.3 ng L^{-1} with an average of 3.1 ng L^{-1} ± 2.2 ng L^{-1} in snow. This partitioning is similar to our first Hg determinations in surficial waters of several lakes in this program (Fitzgerald and Watras 1989), and has been commonly observed in the lakes associated with the current study. With reference to Figures 2 and 3, this difference is not due to MMHg as the MMHg concentrations (<5 to 224 pg L^{-1}) are considerably smaller than the measured differences between Hg_R and Hg_T. Rather, the partitioning is most probably indicative of Hg associated with atmospheric particulates, some of which may be strongly bound to organic substances. It further signifies the important role of particulate-associated Hg in the biogeochemical cycling of Hg in lakes.

While we are planning additional speciation studies in precipitation, it is important to stress the potential significance of the reactive fraction to the biogeochemical cycling of Hg in aquatic systems. The determination of Hg_R may yield a quantitative measure of the environmentally active (Hg II) substrate. The Hg (II) substrate represents the sum of the readily reducible Hg species at a pH of ca. 1, and it will be composed of labile inorganic (e.g. Hg^{2+} ; $Hg(OH)_2$), organic associations (e.g. simple amino acid Hg complexes) and labile particulate Hg associations. We speculate that these labile chemical forms of Hg provide the active substrate for a range of synergistic and competitive chemical and biologically mediated reactions which include the reduction to Hg^o and the synthesis of MMHg. Further, the source of Hg_R in the rain is most probably due to an atmospheric oxidation or gas/solution oxidation process that depends on the relatively stable elemental concentration in the atmosphere.

The MMHg concentrations in rain varied between 59 and 224 pg L^{-1} with a mean and S.D. of 156 ± 68 pg L^{-1}. These concentrations are consistent with the atmospheric measurements which, as noted, are generally below our detection limit of < 5 to 10 pg m^{-3}. This can be demonstrated in the following manner. We assume that the most probable MMHg species is MMHgOH (Stumm and Morgan 1981) with a value for its Henry Law Constant (H) at 15° C, of 1.7 x 10-7 for $MMHgOH_{(g)}/MMHgOH_{(aq)}$ (Iverfeldt and Persson 1985). Using the average concentration of MMHg in rain (156 pg L^{-1}), and H = 1.7 x 10-7 at 15° C, we obtain a predicted equilibrium tropospheric concentration of $MMHgOH_{(g)}$= 0.03 pg m^{-3}. This concentration is lower than our current detection limit of 5 pg m^{-3} and consistent with the atmospheric observations. A similar result can be inferred from the MMHg measurements in snowfall. Concentrations of MMHg were small with a range between <5 to 80 pg L^{-1}. The mean concentration was of 58 ± 22 pg L^{-1} (including 2 measurements of < 5 and < 30 pg L^{-1}). An estimate of the MMHg concentration in the atmosphere can be made using a Henry's Law equilibrium calculation in the manner previously described. An atmospheric concentration of $MMHgOH_{(g)}$= 0.003 pg m^{-3} is obtained (Fitzgerald et al. 1991); a concentration well below our current detection limits. Both of these estimates are in accord with the atmospheric Hg speciation results described previously.

LAKE STUDIES

Studies of dissolved gaseous Hg (DGM) were conducted as part of the UCT intensive studies of the air-water exchange of Hg in temperate lakes. As noted in the experimental section, the five study sites ranging in pH from 4.7 to 7.2, have been investigated under a variety of limnological conditions. The pertinent information associated with our investigations of the volatile Hg cycle can be found in Vandal et al. (1991). Here a brief summary of significant observations will be presented. The DGM fraction consists principally of Hg° under all sampling conditions, with no significant contribution from volatile organic Hg species (detection limit of 3 fM). Thus, Hg° has been found to be the principal species of atmospheric gaseous Hg and DGM. In general, the lakes have been supersaturated with Hg° relative to the atmosphere, indicating a flux of Hg° out of the lake (Fitzgerald et al. 1991). Supersaturation was greater in the summer, ranging from ca. 1.4 to 12 x the saturation concentration, than during the other sampling periods when Hg° ranged from saturation to ca. 7 x the equilibrium concentration (Vandal et al. 1991). The estimated evasional fluxes for the different sampling periods are tabulated in Table 3.

DISCUSSION AND CONCLUSIONS

SUMMARY BUDGET: ANNUAL NET ATMOSPHERIC Hg DEPOSITION

The atmospheric Hg flux data can be assessed in a mass balance Hg budget for LRL. A preliminary budget has been published for the treatment basin (Fitzgerald and Watras 1989, Wiener, et al. 1990). The current results allow us to refine the mass balance, constrain the Hg flows, test the data for geochemical consistency and evaluate the implications. Thus:

NET Hg INPUT = WET DEPOSITION (RAIN + SNOW)
+ DRY DEPOSITION ± GASEOUS Hg EXCHANGE (1)

The estimated annual deposition noted for rain (4.5 ± 2.0 μg m^{-2} yr^{-1}), snow (2.3 ± 0.3 μg m^{-2} yr^{-1}) and dry deposition (3.5 ± 3.0 μg m^{-2} yr^{-1}) yield a total Hg deposition of 10.3 ± 3.6 μg m^{-2} yr^{-1} for the temperate lake environs. It is noteworthy that the average deposition is comparable to our measurements of Hg in rainfall from the northeast Pacific Ocean (9 ± 5 ng L^{-1}) which yield an estimated deposition of Hg at 10 μg m^{-2} yr^{-1} (Fitzgerald, 1989).

The evasional fluxes of Hg^{o} are geochemically significant. Vandal et al. (1991) demonstrate the biogeochemical importance of Hg^{o} evasion in temperate lakes using the experimental results from the reference and treatment basins of LRL. Here, we will utilize their final results by referring to their work for pertinent data, geochemical assumptions and other relevant details associated with the flux calculations. Thus, the estimated evasional Hg^{o} flows to the atmosphere from LRL are presented in Table 3.

Although, these estimates are order of magnitude approximations, they provide a basis to assess the potential importance of evasional Hg^{o} losses to the overall cycling of Hg in lacustrine environments. Firstly, the evasional Hg^{o} fluxes are quite significant yielding an average range from 7 to 14 % of the estimated total atmospheric Hg deposition to LRL at 10.3 ± 3.6 μg m^{-2} yr^{-1}. Secondly, if we focus on the temporal or seasonal situation, the fluxes in August are much larger than in October (Table 3). Thirdly, and perhaps most importantly, the flow from the reference basin is, in general, greater than the evasional losses from the treatment basin. This suggests a potential amelioration role associated with the production and evasion of Hg^{o} from lakes. That is, the transport of Hg^{o} from the lake surface to the atmosphere can play an important role in reducing the amount of Hg in the aqueous pool. It also suggests a mechanism that might lead to increased levels of Hg in lakes affected by increasing acidity. Additional speculation might include the notion that less sheltered water bodies with an enhanced gas exchange at the water-air interface may have biota with lowered MMHg levels.

Table 3. Evasional Fluxes of Elemental Hg from Little Rock Lake.

	---------- Evasional Fluxes ----------	
Little Rock Lake	Reference Basin	Treatment Basin
October, 1988 ng m^{-2} d^{-1}	6.4	2.5 ± 0.3
August, 1989 ng m^{-2} d^{-1}	10.4 ± 5.5	5.0 ± 2.5
Annual Flux μg m^{-2} yr^{-1}	1.5 ± 0.9	0.7 ± 0.3

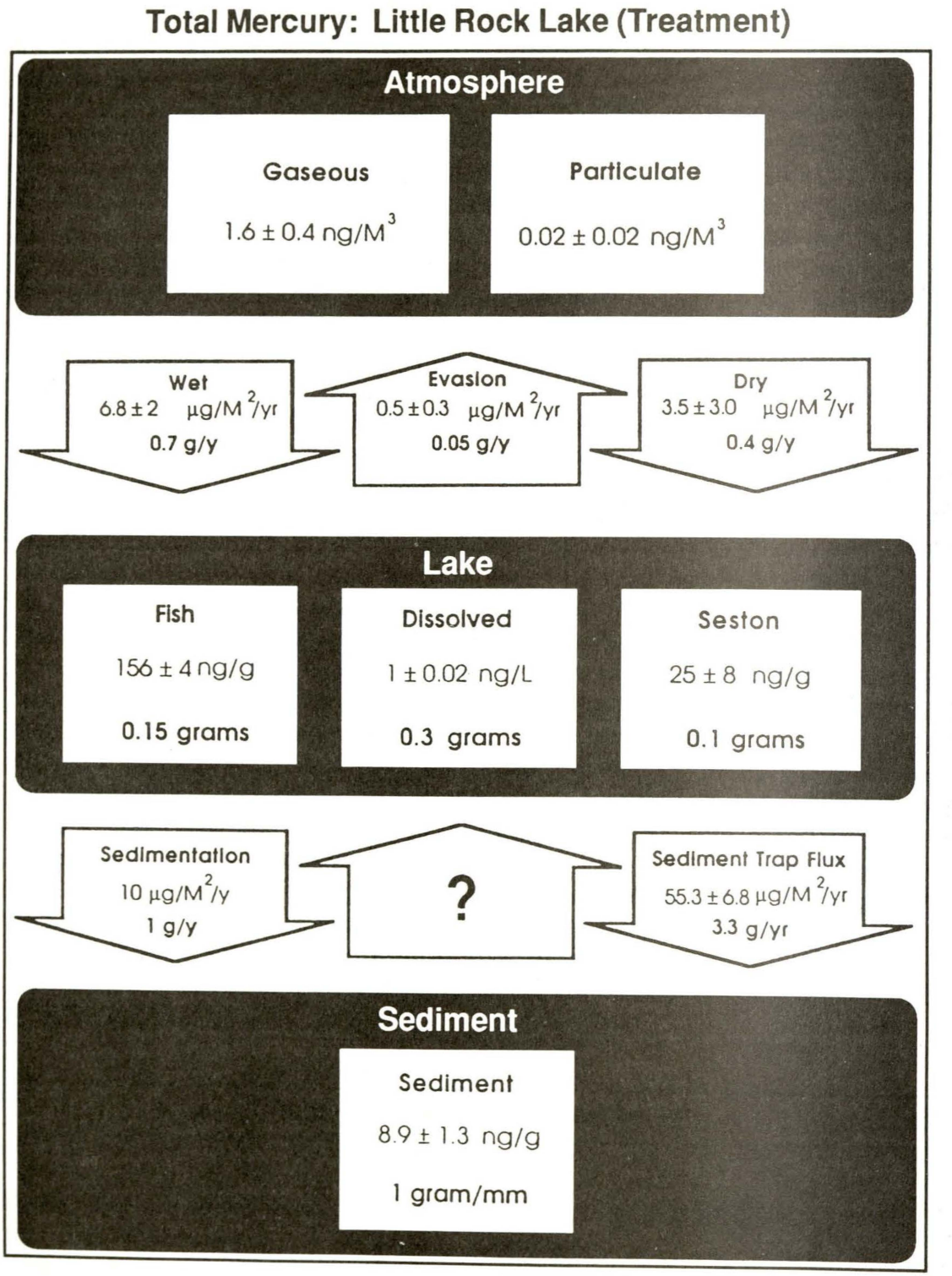

Figure 4. Mass balance for Hg in the treatment basin of Little Rock Lake, WI (adapted from Watras et al. (in preparation), Wiener et al. 1990, Fitzgerald and Watras 1989).

There is sufficient information to allow LRL to be used as an analog for the Hg cycling in temperate seepage lakes. Thus, we find atmospheric Hg deposition (ca. 66% wet and 34% dry) can readily account for the total mass of Hg in fish, water and accumulating in sediment of Little Rock Lake. A mass balance developed for the treatment basin is shown in Figure 4. The Hg contents for the various compartments were obtained from the following sources: the data for the fish and sediment were taken from Wiener et al. (1990), and the data for the water and seston were obtained from Watras et al. (in preparation). This mass balance is well constrained since the inputs of Hg adequately match the estimated accumulation of Hg in the sediment. This analysis highlights a number of significant features of the biogeochemical cycling in these aqueous environments.

The scaling indicates that modest increases in atmospheric Hg loading could lead directly to elevated levels in the fish stock. For example, if we assume that the yearly turnover in fish biomass containing 0.15 g of Hg as MMHg were ca. 40%, then about 0.06 g Hg would be needed. This amount of Hg is <10% of the annual net input. Thus, the ecosystem appears delicately poised with respect to atmospheric inputs, since a relatively small fraction of the input readily accounts for the estimated accumulation of Hg in fish.

A less refined estimate for the supply of MMHg from the atmosphere can be developed with the mean concentrations observed in snow and rain. Thus, rain and snow deposition yields 66 ± 28 and 22 ± 8 ng m^{-2} yr^{-1}, respectively, for an annual flux of 88 ± 29 ng m^{-2} yr^{-1}. While no dry deposition information is available, these preliminary data for the atmospheric deposition of MMHg suggest that this flux is insufficient to account for the amounts of MMHg observed in biota. Approximately 0.01 g of MMHg is delivered to the treatment basin annually. This flux is about 15% of estimated yearly MMHg accumulation in the fish stock. An in-lake synthesis of MMHg is implicated.

REACTIVE Hg(II) SUBSTRATE HYPOTHESIS

As noted, the evasional fluxes of Hg° are significant. Moreover, the effluxes are greater from LRLR as compared to LRLT. This indicates that increasing acidity may reduce the in-lake production and efflux of Hg° . The total Hg concentrations and burdens in whole age-1 yellow perch are greater in the treatment basin relative to the reference side (Wiener et al. 1990).

This is consistent with the physicochemical concept that in-lake biological and chemical production processes for Hg° and MMHg may be in competition with one another for the reactive Hg substrate existing as labile Hg (II) species. We suggest that once Hg° is produced in the aqueous phase, it is unreactive and eventually lost from the system. Thus, lakes with limnological conditions favoring Hg° production would be less likely to have elevated levels of Hg in the fish stock.

The potential importance of the processes leading to in-lake syntheses of Hg° and their influence on MMHg production can be illustrated by comparing the effluxes of Hg° with the input of reactive Hg rather than the total Hg input. Most of the Hg in wet deposition appears to be

associated with particulate matter and these forms of Hg may not be readily available for either methylation or the synthesis of Hg^0 . The average reactive Hg is ca. 30% of the total Hg in wet deposition and if we assume that this fractionation would apply to the particulate phase as well, then an estimate of the annual reactive Hg flux is 3.0 $\mu g\ m^{-2}\ yr^{-1}$. We contrast this value with the estimated Hg^0 of 0.7 ± 0.3 $\mu g\ m^{-2}\ yr^{-1}$ for the treatment basin and find a most significant reduction (ca. 23%) in the Hg readily available for methylation. We note with emphasis that the Hg^0 efflux from the reference basin at 1.5 ± 0.9 $\mu g\ m^{-2}\ yr^{-1}$ is ca. twice the flux from the treatment basin and about 50% of the reactive Hg input.

A further indication of the biogeochemical importance of the aquatic Hg^0 cycle can be gained from a comparison of the estimated annual in-lake net production of Hg^0 and MMHg in the treatment basin. Thus, from Figure 4, we assume that the average yearly evasional Hg^0 flux of 0.07 g is equivalent to annual net in-lake Hg^0 production. In a similar manner, we assume that the estimate of 0.06 g for the net annual accumulation of MMHg in biota represents the net yearly in-lake production of MMHg. It is strikingly evident that these fluxes are of the same magnitude.

Finally, the Hg(II) substrate hypothesis should also be viewed in the most general physiochemical manner. Although, for example, "methylating and reducing processes" utilize Hg (II) species, this active substrate can be rendered inactive by strong sequestering with organic ligands. In some circumstances, perhaps inorganic interactions (e.g. with S) could reduce the activity of the active substrate. We note that aspects of the Hg(II) substrate hypothesis were suggested by Fagerstrom and Jernelöv (1972). While these scaling exercises establish the potentially important role of Hg^0 production in lakes and other natural waters, our present understanding of the mechanisms associated with its synthesis is very sparse.

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METAL TOXICOLOGY AND FISH DEVELOPMENT

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ABSTRACT.- The early life stages of an animal's life cycle are the most sensitive to environmental contaminants. Responses of fish embryos and larvae to many metals include mortality, as well as morphological, physiological and biochemical alterations. As teratogens, metals are fairly nonspecific, since the same abnormalities can be elicited by a number of different chemicals. Common morphological abnormalities include optic, skeletal, and cardiovascular malformations. Physiological responses include decreased motility and precocious or delayed hatching. Biochemical effects are reflected in reduced or inhibited enzymatic activity and reduced growth. Larval studies have usually been restricted to observations of mortality. Salmonids tend to be among the most sensitive species, responding to some metals at, or less than, one $\mu g\ L^{-1}$. In fish, metal interactions with salinity, pH, and temperature have been noted as well as interactions between toxicants. Interactions between metals can be additive or antagonistic.

INTRODUCTION

Developmental toxicity is a broad term, encompassing abnormal development (teratogenicity), mortality, growth inhibition, and functional deficiencies during early life stages. Embryonic and larval stages are often the most sensitive periods in the life cycle of aquatic organisms, responding to subtle chemical and physical changes in the environment. Furthermore, there are toxicants that exert their effects particularly on developing systems.

Aquatic environments are the ultimate repository for pollutants, whether by point-source effluents, non-point source runoff or by atmospheric deposition. Accordingly, there are many studies of reproductive and developmental effects of environmental pollutants on aquatic biota. In addition to studies of the nature and degree of abnormalities produced, there are attempts to analyze mechanisms of action of the teratogens. The effects studied include not only embryonic malformations but also effects on developmental processes that occur at later life stages, such as hatching and larval growth.

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When considering the developmental toxicity of metals, attention must be given to the fact that some of these elements are essential micronutrients for which toxicity thresholds tend to be two or three orders of magnitude greater than that of non-essential elements. That is, while embryos of a given species may be sensitive to nanomolar concentrations of such non-essential metals as Cd and Hg, micromolar concentrations are necessary to elicit a toxic response to Cu and Zn. Another facet of metal toxicity to be considered is the speciation of the metal. For example, Cr(VI) is substantially more toxic than Cr(III), and is the more prevalent species in seawater. A third facet in metal toxicity is alkylation. Organometals are frequently much more toxic than their inorganic counterparts. This is generally because the alkyl group reduces solubility and the resultant hydrophobic (and thus lipophilic) molecule penetrates cell membranes (lipid bilayers), and thus gill and gastrointestinal epithelia, more readily.

Typically, experimental fish embryos are exposed to metals after fertilization. However, embryos in the natural environment can be exposed to pollutants in two additional ways: via yolk which is synthesized during oogenesis by exposed females, and during the brief period (at most, a few minutes) between shedding of the gametes and elevation of the chorion. A few studies have shown that metals incorporated into the egg during oogenesis can produce malformations in the embryos that subsequently develop from those eggs (Zn - Speranza et al 1977; Hg - Birge et al 1979, and McKim et al 1976). Once the chorion is elevated and hardened, it can act as a barrier to partially protect the developing embryo from the toxic effects of many pollutants (Ozoh 1980).

MECHANISMS OF EFFECTS OF DEVELOPMENTAL TOXICANTS

TERATOGENIC EFFECTS

It is an axiom of teratology that a defect in morphogenesis of a structure can occur if a teratogenic insult is present during the "critical stage" of development of that structure, the critical stage being the sensitive period of tissue differentiation and rapid growth. Different substances can produce similar deformities if present at the critical stage, even though the actual modes of action of the different chemicals may differ. Teratogens thus tend to be fairly non-specific in the nature of the defects that they cause (Laale 1981). Mechanisms that can lead to abnormal development include: abnormal cell or tissue differentiation, excessive, or inadequate cell death during development, inadequate cell migration, improper cellular communication, and disrupted metabolism (respiration, absorption, excretion, or secretion).

Fish embryos tend to become abnormal in certain ways. The most sensitive system appears to be the developing skeletal system, and flexures (scoliosis, lordosis) as well as stunting are seen in many species treated with a variety of teratogens. Another common set of abnormalities involves the developing circulatory system. Circulatory stasis, a failure of the heart tube to bend, and edema of the pericardial cavity are also commonly observed defects. The developing optic system is also very sensitive, and many investigators have observed optic malformations, such as microphthalmia and anophthalmia, as well as cyclopia and intermediate conditions of fusion of the two optic vesicles (synophthalmia). Again, these tend to be non- specific responses; the

appearance of a certain syndrome in a certain species of fish cannot in general be used to diagnose the presence of a specific teratogen.

Although not strictly a developmental anomaly, another phenomenon often observed in teratogen-exposed embryos is a general retardation of development. This decrease in developmental rate, or, sometimes, arrest of development may permit teratogens to act for longer than normal time during critical stages, and thus intensify the severity of the resultant anomalies. Developmental arrest in itself will not cause abnormalities if recovery occurs and normal development resumes. Laale and McCallion (1968) found that homogenates of zebrafish *(Brachydanio rerio)* embryos caused intact embryos to arrest their development. Upon return to fresh water, the embryos resumed normal development. Therefore, it is not the developmental arrest itself, but the continuous exposure to a teratogen at that critical time, that causes the anomalies once development resumes. Conversely, environmental or inherent factors that enable embryos to develop more rapidly, spending less time at critical stages, can make them less susceptible to teratogenic influences (Weis et al 1981b; Toppin et al 1985).

PHYSIOLOGICAL AND BIOCHEMICAL EFFECTS

Many heavy metals have been shown to act specifically by inhibiting certain enzymes, thus interfering with metabolic processes in development. Divalent cations can cross-link sulfhydryl groups and thereby disrupt (denature) the tertiary structure of enzymes, rendering them less active or inactive. Such events may result in teratogenic responses, but sometimes an organism exhibits less dramatic but nevertheless serious consequences, especially if the exposure occurs outside the critical stages. Such sequellae include diminished or retarded growth, inhibited, delayed or precocious hatching, or outright mortality.

DEVELOPMENTAL TOXICITY OF SELECTED METALS

MERCURY

Mercury, a non-essential element, finds its way into the aquatic environment via industrial effluents and atmospheric deposition. Abnormalities in the development of the optic cups have been observed by many investigators. Dial (1978b) observed disorganized retinas, abnormal pigment distribution, and invasive blood sinuses in eyes of medakas (*Oryzias latipes*) treated with 80 $\mu g\ L^{-1}$ methyl-Hg. There was also evidence of mitotic arrest. Many investigators, starting with Stockard (1907), have noted a defect in forebrain development in which the eye rudiments converge, sometimes to the point of cyclopia. The cyclopic eye noted by Weis and Weis (1977a,b) in $HgCl_2$ and methyl-Hg treated mummichog (*Fundulus heteroclitus*) embryos exhibits an unusually large optic cup and lens (Figure 1), since it is the result of the fusion of the two separate rudiments. The mechanism underlying the fusion of the optic vesicles is believed to be an inadequate induction of the forebrain, which then allows the convergence of the two vesicles in the anterior midline of the embryo. This anomaly, therefore, is not strictly an optic one -

rather, its genesis involves a defect in craniofacial development. The organic Hg was effective at one-third the equivalently effective concentration of inorganic Hg ($HgCl_2$) in this species.

Fundulus is also susceptible to cardiovascular anomalies, ranging from a slight inhibition of morphogenesis of the heart, through a contracting but undifferentiated simple tube, to complete failure of cardiovascular development. Both organic and inorganic Hg compounds will bring about these cardiovascular anomalies in *F. heteroclitus* (Weis and Weis 1977a,b) as does $HgCl_2$ in *O. latipes* (Heisinger and Green 1975). In the latter species, Dial (1978a,b) noted failure of the incorporation of the heart into the body after five days exposure to 40 $\mu g\ L^{-1}$ methylmercury. Other abnormalities included stunting, reduced pectoral fins, and reduced pigmentation. Those embryos that hatched exhibited erratic swimming, indicating neurological effects.

Skeletal anomalies - flexures and stunting - have been observed in *F. heteroclitus* treated with Hg compounds (Sharp and Neff 1980; Weis and Weis 1977a,b) and *O. latipes* treated with methyl-Hg (Dial 1978a,b). Birge et al (1979) noted immobile jaws, partial twinning, and rigid coiling in treated rainbow trout (formerly *Salmo gairdneri*, now *Oncorhynchus mykiss*.) They noted that terata are a much more common response in some species than others, being commonly seen in treated rainbow trout, but much less often seen in treated channel catfish (*Ictalurus punctatus*), goldfish (*Carassius auratus*), or largemouth bass (*Micropterus salmoides*). These latter species more commonly responded with mortality rather than with abnormalities. In a study of six metals and metalloids, Birge et al (1983) exposed rainbow trout embryos and found that Hg (both organic and inorganic) was the most toxic and teratogenic. The LC_{50} was 5 $\mu g\ L^{-1}$ and both mortality and terata were elevated at as little as 1 $\mu g\ L^{-1}$ of either organic or inorganic Hg. This is an example, sometimes seen in freshwater fish, of inorganic Hg being as toxic as the organic form. Also, this report demonstrates the extreme sensitivity of salmonid species to teratogens.

Weis et al (1982) found differential responses to $HgCl_2$ by embryos in two populations of *Fundulus*. One population responded to 50 $\mu g\ L^{-1}$ with a moderate degree of teratogenic responses, primarily the craniofacial, cardiovascular, and skeletal abnormalities described above. The other population (which was from a highly polluted environment and had acquired increased resistance to methyl-Hg induced teratogenesis) responded to $HgCl_2$ exposure with high mortality but not a high incidence of abnormalities.

Exposure of adults to Hg has been investigated in relation to the developmental effects on offspring. Brook trout (*Salvelinus fontinalis*) transferred Hg from adult tissues to developing oocytes, resulting in some malformations (McKim et al 1976). Birge et al (1979) treated adult rainbow trout with 0.2 and 0.7 $\mu g\ L^{-1}$ Hg and raised fertilized eggs from these chronically exposed fish in clean water. Larval survival at four days post-hatching was less than 50%, and many of the larvae were abnormal. Mortality rates were higher for the embryonic stages than for the larvae. A significant reduction in reproductive success, i.e., increased mortality and abnormalities, was also noted for adults chronically exposed to 0.2 $\mu g\ L^{-1}$ Hg. The authors felt their data indicated that the freshwater criterion of 0.05 $\mu g\ L^{-1}$ Hg may not adequately protect reproduction in salmonid species.

Critical periods in development were considered in several studies with Hg. Gastrulation is the critical period in *Fundulus* for the genesis of craniofacial defects by methyl-Hg (Weis and Weis 1977b). This corresponds to the time of induction of the forebrain, defects in which are believed responsible for the convergence of the optic cups. Akiyama (1970) identified early cleavage and the time of brain and optic vesicle formation as the times of highest susceptibility of *O. latipes* to two organic Hg compounds, phenylmercuric acetate and methoxyethylmercuric chloride.

Perry et al (1988) observed decreased mitotic index and increased percentage of abnormal mitoses in methyl-Hg treated embryos of *F. heteroclitus*. Embryos with more severe teratogenic responses had more severe mutagenic responses.

In a study of biochemical effects of methyl-Hg in *S. fontinalis* embryos, Christensen (1975) noted a decrease in glutamic oxalacetic transaminase after exposure to 1.03 $\mu g\ L^{-1}$. Alevins showed decreased weight and increased enzyme level.

Varying the salinity alters the susceptibility of embryos to toxic effects of pollutants. Decreased salinity increased the toxicity of methyl-Hg to *F. heteroclitus* (Weis *et al* 1981b). However, Sakaizumi (1980) found that exposure of medaka embryos to methylmercury in a salt solution (Yamamoto's solution) reduced hatching to a greater extent than comparable exposure in deionized water. When various inorganic salts were tested, only halides were found to reduce hatching while nitrate and sulfate had no effect. At the same time, these halides (Cl and Br) were found to reduce the uptake of mercuric chloride and methylmercuric chloride into the yolk of the embryos, while uptake into the embryo proper was increased, thus accounting for the intensified effects.

CADMIUM

Cadmium, like mercury, is non-essential, and its effects on fish development have been widely reported. Effects of Cd on embryos and larvae of seven freshwater fish species (*Salvelinus fontinalis, Salmo trutta, Salvelinus namaycush, Oncorynchus kisutch, Esox lucius, Catostomus commersoni* and *Micropterus dolomieui*) were studied by Eaton et al (1978). Of the embryos, only those of the white sucker (*C. commersoni*) were not able to tolerate the highest test concentration ($100\ \mu g\ L^{-1}$). The chorion apparently confers protection. Thus, larvae were consistently more sensitive than the embryos and showed diminished growth. This may be due to decreased enzyme activity, which has also been noted in Cd-exposed embryos. Mounib et al (1975) found that Pacific herring eggs exposed to $10\ mg\ L^{-1}$ Cd showed decreases in NAD and NADP-malic enzymes, propionyl-CoA-carboxylase, and phosphoenol-pyruvate carboxykinase, enzymes that are involved in biosynthetic processes.

Cadmium at $239\ \mu g\ L^{-1}$ produced pericardial edema, delayed yolk resorption, microcephalia, and skeletal malformations in the bluegill (Eaton, 1974). Skeletal malformations were seen in medaka embryos treated with 10 and $50\ \mu g\ L^{-1}$ cadmium (Hiraoka and Okuda 1983).

Cadmium treatment of the rainbow trout *O. mykiss* at 10 and 100 μg L^{-1} produced classical cardiac malformations, premature hatching, retarded growth and increased rates of mortality (Woodworth and Pascoe 1982). In this study, exposures started at 19 days after fertilization, so early developmental effects could not have been detected. Rombough and Garside (1982) studied effects in the Atlantic salmon, *Salmo salar*, and found that, although the eggs take up Cd rapidly, the alevin growth was much more sensitive, being affected at 0.47 μg L^{-1} while the LC_{50} for embryos was 300-800 μg L^{-1}. Gastrulation, axiation, the time of development of vitelline circulation, and the period just before hatch were the most sensitive embryonic stages. High concentrations produced skeletal malformations. The embryonic toxicity appeared to be greater at 5° C than at 10° C. This may have been due to a prolongation of sensitive stages by the reduced developmental rate at the lower temperature. However, increased temperature increased the toxicity of Cd to embryos of the fathead minnow in a short term embryo-larval test (Birge et al 1985). Cadmium was also more toxic at 10° C than at 5° C to winter flounder (*Pseudopleuronectes americanus*) embryos (Voyer et al 1977). These latter reports suggest a metabolic effect and differ from the greater teratogenic effects usually seen in other systems at reduced temperatures.

Some studies have noted that a very small percentage of the Cd actually reaches the embryo. Beattie and Pascoe (1978) found that in rainbow trout embryos, 98% of the Cd was associated with the chorion, rather than with the embryo itself or the yolk. Peterson et al (1985) found that 90% of the Cd uptake by salmon embryos was associated with the chorion. Similarly, Michibata (1981a) found that over 94% of the Cd in medakas was found in the chorion, and Rosenthal and Sperling (1974) found over 60% of the Cd in herring eggs was in the chorion.

Decreased salinity increased the toxicity of Cd to winter flounder embryos as measured by viable hatch (Voyer et al 1977). The enhanced toxicity at lower salinity may be due to greater uptake of water, and, therefore, of the toxicants. The optimum salinity for resisting Cd effects was 20-25 parts per thousand (ppt), a salinity typically found in this species' spawning grounds. Similarly, reduced salinity intensified the effects of Cd on herring embryos (*Clupea harengus*) (Westernhagen et al 1974). Prehatching mortality and malformation rates (skeletal bending, stunting, reduction in otic capsule and otolith size, optic size), and behavioral abnormalities after hatching were highest at low salinities. The chorion was softened in the Cd-treated embryos. The optimal salinity was 25 ppt and Cd uptake was greater at lower salinities. At these lower salinities, more of the Cd is available as free ions (the toxic form) and less would be complexed. A comparable situation in freshwater systems is hardness; increased water hardness reduces the uptake of the Cd and thus reduces its toxicity to *O. latipes* embryos (Michibata 1981b). More recently, Michibata et al (1986) analyzed the effect of water hardness by studying the effects of Ca and Mg separately in Cd-exposed medaka eggs. Calcium, but not Mg, was able to reduce the acute embryotoxicity by 80%. However, the reduction in Cd uptake brought about by Ca and Mg was similar. The authors concluded that since 94% of the bound Cd was associated with the chorion, very small changes in total uptake could account for the significant changes in toxicity to the embryo proper.

Similarly, pH had a major influence on Cd uptake and toxicity in Atlantic salmon (*Salmo salar*) (Peterson et al 1985). At lower pH levels, more Cd was available for embryonic uptake due to

lowered chorionic binding. On the other hand, Dave (1985) studied effects of Cd and pH on embryos and larvae of *B. rerio* and found that Cd was more toxic at higher pH levels. Survival was not impaired for the first three days of Cd exposure up to 4.1 mg L^{-1} at any pH, but after hatching survival was reduced at concentrations as low as 30 µg L^{-1} with the most toxic pH being 6-7 and the least toxic being 9.0. It should be noted that in this study embryonic exposures did not start until the optic cup stage, past the most sensitive embryonic stages.

COPPER

Copper is a required micronutrient; nevertheless, many species of fish are sensitive to its toxic effects at relatively low concentrations. Herring (*Clupea harengus*) eggs had high mortality when incubated in 30 µg L^{-1} Cu (Blaxter 1977). Those larvae that hatched in 30 µg L^{-1} were deformed. If exposure was initiated four days after fertilization, deformities were not apparent, indicating that the early embryonic stages included the critical stages. Copper exposure tended to accelerate the hatching rate. Larvae were 30X less susceptible than the embryos.

McKim et al (1978) studied effects of Cu on the embryos and larvae of eight species of freshwater fish (*Catostomus commersoni, Coregonus artedi, Salvelinus fontinalis, S. namaycush, Salmo trutta, Onchyrhynchus mykiss, Esox lucius*, and *Micropterus dolomieui*.) Larvae and juveniles were all more sensitive than embryos. Embryo survival was affected only at the higher concentrations tested (northern pike at 500 µg L^{-1}, rainbow trout at 37 µg L^{-1}, white sucker at 333 µg L^{-1}, brook trout at 555 µg L^{-1}, lake trout at 555 µg L^{-1}, brown trout at 111 µg L^{-1}, and herring at 555 µg L^{-1}.) No effect was seen on smallmouth bass embryos at any concentration tested. However, embryonic exposure reduced the larval resistance to Cu; brown trout that were exposed for the longest embryonic period were the most sensitive as larvae. Benoit (1975) found that in the bluegill, larvae were also more sensitive than embryos; 77 µg L^{-1} had no effect on the embryos but did reduce larval survival. He also observed that larvae at 12 µg L^{-1} survived better than the controls, which may be an example of hormesis (overcompensation by regulating mechanisms after exposure to a low concentration of a toxicant.)

Rice et al (1980) also found that embryos of the northern anchovy, *Engraulis mordax*, were more sensitive than larvae, and indicated that, in general, larvae of freshwater fish are more sensitive than embryos, while embryos of marine fish are more sensitive than their larvae. Salmon, living in the ocean but spawning in fresh water, behave like saltwater fish in this regard.

Engel and Sunda (1979) compared the sensitivities of embryos of the spot, *Leiostomus xanthurus*, which has planktonic eggs, and the silversides, *Menidia menidia*, which has demersal eggs, to Cu concentrations, measured as the free ion (pCu) in a buffer system. They found the silversides were more sensitive in terms of hatching success, which was surprising since they had considered planktonic eggs to be more delicate than demersal eggs. For the silversides, the greatest toxicity occurred at the time of hatch; the greatest mortality of spot took place prior to hatch.

Copper concentrations of 10 µg L^{-1} and higher increased mortality of embryos, decreased hatching frequency, prolonged incubation time, and produced abnormalities in developing cod (*Gadus*

morhua) embryos (Swedmark and Granmo 1981). Among the abnormalities noted at 10 µg L^{-1} were bent axis and cyclopia. Copper toxicity was reduced by the surfactant LAS, a chemical that when used alone, had about the same level of toxicity as the Cu.

ZINC

Zinc is another required micronutrient which can be embryotoxic above naturally occurring concentrations. Bengtsson (1974) found that Zn exposure caused vertebral damage in the minnow, *Phoxinus phoxinus*. In the zebrafish (*B. rerio*), exposure to 1 and 2 mg L^{-1} Zn caused damage to the vertebral centra and deflection of the caudal peduncle in medaka (Birge et al 1985). Holcombe et al (1979) found that exposure to 1.4 mg L^{-1} Zn decreased embryo survival and chorionic strength in the brook trout. The latter effect may be ecologically important in this species since the eggs are normally buried in gravel. The effect was greater in eggs that were transferred to Zn prior to chorionic hardening. Similarly, Benoit and Holcombe (1978) found that 145 µg L^{-1} Zn exposure of newly fertilized fathead minnow eggs caused a decrease in egg adhesiveness and increase in their fragility. At 295 µg L^{-1}, skeletal deformities were observed, and hatchability and larval survival were diminished. No deleterious effects of Zn exposure of 240 µg L^{-1} were seen in egg to smolt stages of the sockeye salmon, *Oncorynchus nerka*. Rather, a slight stimulation of growth was seen (Chapman 1978). This may be another example of hormesis.

Speranza et al (1977) observed malformations in offspring of *B. rerio* adults previously exposed to Zn. Thus, Zn accumulated in the adult tissues could be transferred to the eggs during oogenesis, causing the developmental defects.

Embryonic exposure to Zn increased larval Zn resistance in the flagfish, *Jordanella floridae* (Spehar et al 1978). Preexposure to a low concentration of the metal thus resulted in enhanced tolerance. Induction of metal-binding proteins, such as metallothionein, is one mechanism by which this can occur.

ARSENIC

Arsenic has micronutrient value but is toxic above trace levels. It is also carcinogenic, mutagenic and teratogenic. It exists in four oxidation states, of which two, As(III) and As(V), are prevalent. Of these, As(V) is the more prevalent and less toxic. Arsenic is associated with certain metallic ores, so it can be an environmental problem near smelters. Fortunately, bioconcentration factors are relatively low (Eisler 1988). The studies of As effects on fish embryos that have come to our attention include two on rainbow trout embryos. In one, a 28-day LC_{50} of 0.54 mg L^{-1} and no teratogenic response was reported (USEPA 1980). In the other, Birge et al (1983) found skeletal malformations at concentrations as low as 0.25 mg L^{-1}. In the latter study, the use of As(III) was specified.

SELENIUM

Selenium, a required micronutrient, is of special interest to toxicologists because of its antagonistic interactions with some toxic heavy metals, especially Hg. It is toxic by itself. When, bluegills (*Lepomis macrochirus*) were exposed to 30 ppm dietary Se (as Se-methionine or as selenite, the predominant organic and inorganic forms), the F_1 larvae were edematous and had excess skeletal anomalies and subsequent mortality. The organic Se was much more toxic than the inorganic Se, producing 100% mortality and 100% terata vs. 25% and 15%, respectively (Woock et al 1987). Bluegills taken from a Se contaminated reservoir had offspring with similar defects (Gillespie and Baumann 1986). In a study in which Se (as selenate) was added to rearing water, rainbow trout embryos showed mortality at concentrations as low as 10 $\mu g\ L^{-1}$. Teratogenesis was not obvious below 1 mg L^{-1} (Birge et al 1983).

METAL-METAL INTERACTIONS

In most polluted environments, multiple pollutants would be expected to be found, rather than one single chemical. Thus, interactions between and among metals could be expected. Some of these possible interactions have been studied in developing fish embryos. Many of such studies with metals have shown antagonisms, in that the toxicity of one metal was reduced by the presence of the other. Zinc reduced the teratogenic effects of methylmercury on *F. heteroclitus* (Weis et al 1981b) and Se reduced the toxicity of Hg to medaka embryos (Bowers et al 1980). In the latter study, anomalies produced by $HgCl_2$ included lack of hemoglobin and blood circulation, abnormal heart development, and malformations in the tail region. Selenium, which had no effect by itself, did not reduce the Hg effects until after the embryos' livers had developed, suggesting an important role of that organ in Se protection against Hg toxicity. Klaverkamp et al (1983) studied the interactions of $HgCl_2$ and Se on salmonid (*Onchorhynchus mykiss* and *Salvelinus namaycush*) eggs and found that up to 10 mg L^{-1} Se had no effect on Hg toxicity, but that 100 mg L^{-1} Se did have a protective effect in lake trout eggs. Conversely, Huckabee and Griffith (1974) found a marked synergistic effect between Hg and Se in carp eggs. The failure of Se to protect here may have been due to the early stage of the embryos (pre-liver development) at the time of treatment. Birge et al (1979) found that Hg-Cu and Hg-Se combinations were additive to antagonistic at lower exposure levels to eggs of channel catfish, goldfish, largemouth bass, and rainbow trout, while higher concentrations were synergistic. These results may explain some of the discrepancies in the literature. Another explanation may relate to the form of Hg. Baatrup and Danscher (1987) demonstrated that Se will complex with methyl-Hg but not $HgCl_2$ in trout liver. Nearly all (> 90%) of Hg in fish is methylated because of the relative mobility of the alkylated form as well as an *in vivo* methylating process (Westöö 1967), although the *in vivo* methylating process is not universal (Huckabee et al 1985).

Interactions of metal ions can also reduce the toxicity of Cd to fish embryos by reducing the bioavailability of the free Cd ion. The presence of another divalent cation can trigger competition, thus lowering the amount of the Cd affecting the embryo. Silver reduced the toxicity of Cd to winter flounder embryos (Voyer et al 1982). Similarly, the presence of Zn

increased the viable hatch of herring eggs in 5.0 mg L^{-1} Cd from 0% to 11.4 %. (Westernhagen et al 1974).

DISCUSSION

There is great variability in the papers in this field, partly because different investigators are using fish embryos for different purposes. Some are using them in screening tests for aquatic toxicity testing in order to arrive at maximum acceptable toxicant concentrations and the like. These studies generally use endpoints of hatching success and may include early larval survival and growth as components of an "embryo-larval test." In some cases, the LC_{50} is the only endpoint of interest. Analysis of the developmental abnormalities is generally not included in such studies, although the fact that abnormal embryos were present is sometimes mentioned in passing. It is true, from the perspective of the population, that hatching success and larval growth and survival are important endpoints. It is also true that for a number of toxicants, larvae are more sensitive than embryos. And, substances can vary greatly in their effects on different species.

Among the most commonly observed end-points in toxicity testing for effects of pollutants on fish embryos is successful hatch. Many factors could account for an embryo failing to hatch, embryonic death being a common cause, but grossly abnormal embryos also fail to hatch. In addition, there are often embryos that appear morphologically normal but do not hatch. These three conditions represent a progressive decrease in severity of effect of the toxicant. Studies that differentiate among these different states are more informative than those that merely report percent hatch.

The sensitive periods in embryonic development are often around the time of gastrulation, when the primary inductive events occur. Another important period is the time in which the liver develops. This organ can synthesize metallothioneins to protect the organism against deleterious effects of certain metals, and can be responsible for enhanced tolerance seen after pre-exposure to low levels of metals.

In mammalian teratology, a field much more intensively studied than fish teratology, it has become clear that functional deficiencies are a more subtle response to toxicants than the production of gross anatomical abnormalities. A considerable amount of attention is now being devoted to the study of "behavioral teratology," i.e., abnormal behavior studied after birth of anatomically normal animals which were exposed to teratogens during their embryonic development. Other than occasional reports of lethargic larvae, there has been little or no attention paid to this aspect of developmental responses of fish embryos to environmental pollutants. It would seem to be an area ripe for study, particularly since there have been numerous studies on direct effects of toxicants on behavior of fishes, including feeding, learning, schooling, and breeding behavior. It is likely that embryonic exposure to low concentrations of certain pollutants will result in effects on behavior that would be seen in later life history stages.

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This proceedings contains 14 invited papers from Canada and the United States on trace metal emissions, trace metal measurement in precipitation and dry fall, regional deposition, and the fate of trace metals in soils, plants,waters, and fish. A summary paper integrates the major findings of each paper.

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Our job at North Central Forest Experiment Station is creating, evaluating, and disseminating information and technology to improve the understanding, management, and use of our natural resources.

As a new generation of forests emerges in our region, managers are confronted with two unique challenges: (1) Dealing with the great diversity in composition, quality, and ownership of the forests, and (2) Reconciling the conflicting demands of the people who use them. Helping the forest manager meet these challenges while protecting the environment is what research at North Central is all about.